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Title page:

Absorption and emission spectra of isomeric tolunitriles

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Abstract. Absorption and emission characteristics of *o*-, *m*- and *p*-tolunitriles in non-polar solvents under different conditions have been investigated in detail. Solvatochromic shifts of band origin of these molecules in non-polar solvents show that their dipole moments in the first excited singlet state are almost the same while its value in the second excited singlet state is larger in the meta- than in the para-isomer. Vibronic analyses of the low temperature absorption, fluorescence and phosphorescence spectra of all the three molecules have provided evidence that these molecules are slightly distorted in the first excited singlet state while the distortion in the phosphorescence emitting triplet state is larger. The data on fluorescence quantum yield and phosphorescence lifetime of the tolunitriles are reasonably interpreted as showing that in these molecules, particularly *m*- and *p*-tolunitrile, the internal conversion rate from the first excited singlet to the ground state is probably large and that the charge transfer character of the triplet state in the *p*-isomer is larger than in the meta.

Keywords. Isomeric tolunitriles; dipole moment; molecular geometry; CT-character; radiative and non-radiative rates.

1. Introduction

Benzonitrile which belongs to C_{2v} -point group exhibits two systems of absorption bands of π, π^* character in the near UV region designated as $^1A_1 \rightarrow ^1A_1$ and $^1B_2 \rightarrow ^1A_1$ and correspond to $^1L_a \rightarrow ^1A$ and $^1L_b \rightarrow ^1A$ transitions respectively under Platt notation. Vapour phase absorption measurements (Hirt and Howe 1948) have led to the conclusion that the first excited singlet π, π^* state of the molecule possesses intramolecular charge-transfer (CT) and local excitation character. According to Eisinger and Knight (1970) the phenyl nucleus acts as an electron donor in the CT-process. Furthermore, LeBel and Laposa (1972) have shown that the phosphorescence emitting triplet state of benzonitrile is a $^3A_1 (\pi, \pi^*)$ level and the molecule in the first excited singlet state is a nearly regular but slightly expanded hexagon, while in the first excited triplet state the molecule is planar but a non-regular hexagon. In connection with the EPR studies of the triplet states of fluorobenzonitriles Wagner and May (1976) observed that the first excited triplet state of benzonitrile is a 1,4-diradical, often referred to as the 'quinonoid' form of the triplet.

Among the substituted benzonitriles, the phosphorescence of three isomeric tolunitriles were studied by Takei and Kanda (1962) who concluded that the emission characteristics of the three molecules should be attributed to the electronic transition

based on resonance between the nitrile group and the phenyl ring. Later, Lui and McGlynn (1975a, b) investigated the absorption and emission characteristics of three isomeric cyanoanisoles and fluorbenzonitriles and observed certain similarities in the variations of spectral characteristics among the corresponding members of the two triads. For example, in each triad, the *p*- isomer has the smallest ${}^1L_a \rightarrow {}^1L_b$ energy gap, highest ${}^1L_b \leftarrow {}^1A$ transition energy with the smallest *f*-value and the lowest ${}^1L_a \leftarrow {}^1A$ transition frequency having the largest *f*-value. These authors, on the basis of their experimental results, concluded that in all the substituted benzonitriles, the phosphorescence emitting triplet states have varying amount of π -character. However, they made no attempt to find out if the geometrics of these molecules are affected in the excited singlet and triplet states.

It is known that the methyl group is a weaker electron donor than either the fluorine atom or the methoxy group and therefore, it would be interesting to investigate if the spectral characteristics of the three isomeric tolunitriles show similar variations as found in the two above mentioned triads. It would also be in order to find out, at least qualitatively, if the excited states of these molecules possess any π -character, whether the geometrics of these molecules in the excited states are altered and how these excited state properties are related to the phosphorescence characteristics of the molecules. With these objectives, the absorption, fluorescence and phosphorescence of the three isomeric tolunitriles in polar and non-polar solvents have been investigated. The results obtained and discussion of these results form the subject matter of the present communication.

2. Experimental

Highly pure samples of *m*- and *p*-tolunitriles were obtained from Koch-Light laboratories (England) and *o*-tolunitrile was procured from Fluka (Switzerland). The samples were distilled several times till no impurity could be detected by the GLC-method. The solvents ethanol, *n*-hexane and methylcyclohexane (MCH) were of spectrograde quality from E. Merck (W. Germany) and they were carefully distilled under reduced pressure before being used in the investigation. De-oxygenated solutions of the tolunitriles of *ca.* 10^{-4} M concentration were prepared by the usual freeze and thaw technique and their fluorescence and phosphorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrofluorimeter equipped with a compensated spectral unit. The phosphorescence life-time (τ_p) was measured following the decay of phosphorescence signal on the chart recorder having a response of 0.3 sec. The fluorescence and phosphorescence quantum yields (Φ_F and Φ_p respectively) in ethanol glass (EtOH) were determined by the standard method using benzonitrile as reference. In the case of MCH glass the ratio of the yields (Φ_p/Φ_F) was computed from the ratio of the areas under phosphorescence and fluorescence spectra respectively. The errors in

3.1 Absorption spectra

Like benzonitrile, all the tolunitriles show two systems of absorption bands in the near uv region. The first system of bands at the lower energy has a low f -value and corresponds to ${}^1L_b \leftarrow {}^1A$ transition while the second system with higher energy and moderately large f -value is attributed to ${}^1L_a \leftarrow {}^1A$ transition. If the CH_3 -group is treated as a single mass point, then in the reduced symmetry C_s of *o*- and *m*-tolunitriles both these transitions are ${}^1A' \leftarrow {}^1A'$ while in *p*-tolunitrile (C_{2v} -point group) the designations of the transitions are the same as in benzonitrile. For each isomer the vapour phase absorption spectra undergo bathochromic shifts in solutions and these shifts for the 1L_a -band are larger than those for the 1L_b -band. The absorption spectra of the compounds recorded in rigid EtOH and MCH glasses at 77 K show slight shifts with respect to those recorded at room temperature but the vibrational structures in the former are more pronounced. The relevant data on the absorption of the tolunitriles are presented in table 1 while their vibrational assignments are shown in tables 3a, b and c. For comparison the vibrational frequencies as determined by Padhye and Varadarajan (1962) from vapour phase absorption measurements on the tolunitriles are included in the relevant tables.

Analysis presented in these tables shows that in the absorption spectra of each of the isomeric tolunitrile molecules in EtOH and MCH glasses, at 77 K there are, besides a few fundamental excited state frequencies, progressions involving the frequencies 730 and 757 cm^{-1} in *o*-tolunitrile, 958 and 996 cm^{-1} in *m*-tolunitrile and 778 and 789 cm^{-1} in *p*-tolunitrile. These frequencies most probably correspond to the ground state ring vibration frequencies 715, 995 and 815 cm^{-1} in *o*-, *m*- and *p*-tolunitriles respectively.

Table 1. Absorption spectral data of benzonitrile and isomeric tolunitriles at room temperature.

Molecule	Phase	1L_a band system		1L_b band system		$\nu({}^1L_a) - \nu({}^1L_b)$ (cm^{-1})
		$\nu_{00}(\text{cm}^{-1})$	f	$\nu_{00}(\text{cm}^{-1})$	f	
Benzonitrile	vapour	44740	—	36500	—	8240
	<i>n</i> -hex	43465	0.22	36221	0.012	
	MCH	43277	0.22	36090	0.012	
	EtOH	43277	0.22	36090	0.012	
<i>o</i> -tolunitrile*	vapour	43855	—	35770	—	8085
	<i>n</i> -hex	44234	0.22	35388	0.019	
	MCH	43655	0.24	35263	0.018	
	EtOH	42540	0.25	35139	0.030	
<i>m</i> -tolunitrile	vapour	44430	—	35806	—	8624
	<i>n</i> -hex	43183	0.24	35451	0.021	
	MCH	43090	0.22	35356	0.018	
	EtOH	42722	0.27	35263	0.025	
<i>p</i> -tolunitrile	vapour	43185	—	36204	—	7981
	<i>n</i> -hex	42181	0.30	35961	0.010	
	MCH	42181	0.30	35864	0.008	
	EtOH	42281	0.28	35821	0.008	

Molecule	Solvent	¹ L _a -band system	¹ L _b -band system	<i>a</i> ³ in (ÅU ³)	Dipole moment <i>D</i>		
		Δ <i>v</i> (cm ⁻¹)	Δ <i>v</i> (cm ⁻¹)		Ground state	¹ L _b	¹ L _a
Benzonitrile	<i>n</i> -hex	1275	279	20	4.10	4.81	5.83
	MCH	1463	410				
	EtOH	1463	410				
μ _e ² -μ _g ² average		1.40a ³ - 10.80	0.35a ³ - 0.71				
<i>o</i> -tolunitrile	<i>n</i> -hex		382	25	3.95	5.07	
	MCH		507				
	EtOH		631				
μ _e ² -μ _g ² average			0.45a ³ - 1.12				
<i>m</i> -tolunitrile	<i>n</i> -hex	1247	355	25	4.25	5.21	6.31
	MCH	1343	450				
	EtOH	1708	543				
μ _e ² -μ _g ² average		1.32a ³ - 11.35	0.41a ³ - 1.18				
<i>p</i> -tolunitrile	<i>n</i> -hex	1004	243	25	4.40	5.23	5.43
	MCH	1004	340				
	EtOH	1181	310				
μ _e ² -μ _g ² average		1.03a ³ - 15.65	0.30a ³ - 0.53				

* Solvent shift Δ*v* = *v*₀₀ (gas) - *v*₀₀ (solution) cm⁻¹.

The frequencies 1214 and 1222 cm⁻¹ in *o*-tolunitrile, 1263 and 1289 cm⁻¹ in the *m*- and 1176 and 1198 cm⁻¹ in the *p*-isomer are believed to represent the valance *v*(C-CN) vibration frequencies in the excited state of these molecules. It should be noted that Padhye and Varadarajan (1962) observed this frequency at 1199, 1251 and 1175 cm⁻¹ in the vapour phase absorption spectra of the *o*-, *m*- and *p*-tolunitriles respectively. In the above the two entries for each compound refer to data from the spectra in the two solvents.

3.2 Fluorescence emission spectra

The tolunitrile molecules exhibit well-defined band origin and structured fluorescence in the rigid MCH and EtOH glasses at 77 K. Since all of them are very similar, the spectra of only one, viz *o*-tolunitrile are reproduced in figure 1. For comparison the corresponding ¹L_b ← ¹A absorption spectra recorded at the same temperature are also shown in the same figure and the fair mirror image symmetry between them is evident. Accordingly, the fluorescence is attributed to the reverse ¹L_b → ¹A transition. From the vibrational analyses of these spectra (only one is presented in table 4) it is found that, as in absorption a few ground state frequencies in addition to a short progression involving ring vibration is observed in each of the tolunitriles. These frequencies are 760

Table 3. Vibrational analysis of the absorption spectra at 77 K.

MCH-glass			EtOH-glass		
$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	assignment	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	assignment
(a) Orthotolunitrile					
35263	0	0,0	35139	0	0,0
35767	504	0 + 504	35576	437	0 + 437
35993	730	0 + 730	35896	757	0 + 757
36485	1222	0 + 1222	36353	1214	0 + 1214
36760	1497	0 + 2 $\times$ 730	36700	1561	0 + 2 $\times$ 757
37298	2035	0 + 730 + 1222	37133	1994	0 + 757 + 1214
37442	2179	0 + 3 $\times$ 730	37539	2400	0 + 3 $\times$ 757
38083	2820	0 + 4 $\times$ 730	38156	3017	0 + 4 $\times$ 757
38376	3113	5 $\times$ 730	38748	3609	0 + 5 $\times$ 757
(b) Metatolunitrile					
35356	0	0,0	35263	0	0,0
35800	444	0 + 444	35640	377	0 + 377
36090	734	0 + 734	36221	958	0 + 958
36352	996	0 + 996	36552	1289	0 + 1289
36619	1263	0 + 1263	37232	1969	0 + 2 $\times$ 958
36991	1635	0 + 734 + 996	38193	2930	0 + 3 $\times$ 958
37302	1946	0 + 2 $\times$ 996			
37582	2226	0 + 996 + 1263			
38266	2910	0 + 3 $\times$ 996			
(c) Paratolunitrile					
35864	0	0,0	35894	0	0,0
36485	621	0 + 621	36419	523	0 + 523
36653	789	0 + 789	36684	778	0 + 778
37040	1176	0 + 1176	37094	1198	0 + 1198
37407	1543	0 + 2 $\times$ 789	37442	1548	0 + 2 $\times$ 778
37796	1932	0 + 789 + 1176	37864	1970	0 + 778 + 1198
38229	2365	0 + 3 $\times$ 789	38229	2335	0 + 3 $\times$ 778
38598	2734	0 + 2 $\times$ 789 + 1176	38598	2704	0 + 2 $\times$ 778 + 1198
38957	3111	0 + 4 $\times$ 789	38974	3080	0 + 4 $\times$ 778
39749	3885	0 + 5 $\times$ 789	39749	3855	0 + 5 $\times$ 778

Vapour phase absorption ν_{00} for a. 35770 cm^{-1} b. 35806 cm^{-1} and c. 36204 cm^{-1} . The excited state frequencies for a. 669, 961 and 1199 cm^{-1} . b. 672, 970 and 1251 cm^{-1} c. 507, 761 and 1175 cm^{-1} (Padhye and Varadarajan).

1171 and 1178 cm^{-1} and 1216 cm^{-1} in the *o*-, *m*- and *p*-tolunitrile respectively. These frequencies in the Raman spectra as reported by Takei and Kanda (1962) are respectively at 1209, 1245 and 1194 cm^{-1} for *o*-, *m*- and *p*-tolunitriles. The two entries have the same connotation as given in the preceding paragraph.

3.3 Phosphorescence emission

Like fluorescence the phosphorescence spectra of the tolunitriles in MCH and EtOH glasses show vibrational structures. These spectra, one of which is shown in figure 2, are

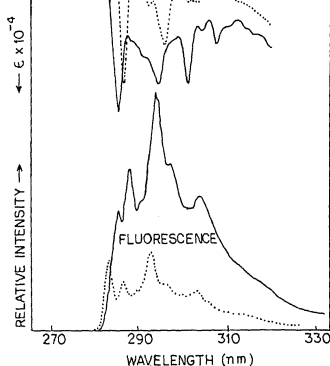


Figure 1. Fluorescence and absorption spectra for *o*-tolunitrile in EtOH (—), and MCH (.....) at 77 K.

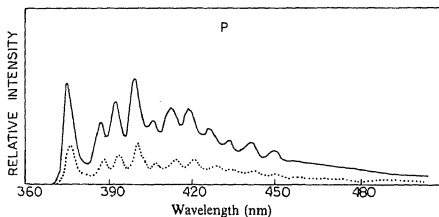


Figure 2. Phosphorescence emission spectra (*P*) of *p*-tolunitrile in EtOH (—) and MCH (.....) at 77 K.

Table 4. Vibrational analysis of fluorescence spectra at 77 K.

EtOH-glass			MCH-glass		
$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	assignment	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	assignment
Orthotolunitrile					
35170	0	0,0	35263	0	0,0
34757	413	0-413	34848	415	0-415
34410	760	0-760	34488	775	0-775
33961	1209	0-1209	34090	1173	0-1173
33618	1552	0-2 $\times$ 760	33703	1560	0-2 $\times$ 775
32872	2298	0-3 $\times$ 760	33323	1940	0-775-1173
			32903	2270	0-2 $\times$ 775

Molecule (medium 77 K)	$K_s \equiv O$								
	ϕ_F	ϕ_p	ϕ_p/ϕ_F	τ_p (sec)	$K_{ISC} \times 10^{-7}$ (sec ⁻¹)	K_p (sec ⁻¹)	$K_{ISC} \times 10^{-7}$ (sec ⁻¹)	K_p (sec ⁻¹)	$S_1 - T_1$ (cm ⁻¹)
<i>o</i> -Tolunitrile									
EtOH	0.36	0.24	0.67	3.40	4.0	0.18	0.24	0.29	8505
MCH			0.51	3.90					8736
<i>m</i> -tolunitrile									
EtOH	0.51	0.23	0.45	4.60	1.4	0.10	0.086	0.22	8795
MCH			0.80	4.40					8961
<i>p</i> -tolunitrile									
EtOH	0.36	0.33	0.92	3.80	2.0	0.14	0.099	0.26	9332
MCH			1.10	3.40					9344
<i>d</i> -fluorobenzonitrile									
EtOH	0.51	0.093	0.18	2.43	1.9	0.077	0.36	0.41	8700
<i>m</i> -fluorobenzonitrile									
EtOH	0.54	0.082	0.15	2.60	1.9	0.068	0.35	0.38	8900
<i>p</i> -fluorobenzonitrile									
EtOH	0.24	0.23	0.96	2.05	2.4	0.15	0.71	0.49	9300
<i>o</i> -cyanoanisole									
EtOH	0.26	0.11	0.42	1.40	14.0	0.11	2.20	0.71	7310
<i>m</i> -cyanoanisole									
EtOH	0.21	0.094	0.45	1.80	15.0	0.066	1.90	0.86	8070
<i>p</i> -cyanoanisole									
EtOH	0.22	0.24	1.00	1.60	10.0	0.18	3.10	0.63	9040

The vibrational assignment of the phosphorescence bands and the second-order magnitude of the phosphorescence lifetime indicate the π, π^* nature of the phosphorescence emitting state in these molecules. Following LeBel and Laposa's (1972) assignment of the phosphorescence emitting state in benzonitrile, which is $^3A_1 (\pi, \pi^*)$, the corresponding state in each of *o*- and *m*-tolunitriles may be designated $^3A' (\pi, \pi^*)$. The data on fluorescence and phosphorescence characteristics are collected in table 5 and for comparison those for cyanoanisoles and fluorobenzonitriles (Lui and McGlynn 1975a, b), are included in this table.

4. Discussion

From the data on the absorption spectra of the three tolunitriles (table 1), it is seen that the *p*-isomer shows spectral features which are different from those of the other two. For example, the 1L_b -band in *p*-tolunitrile has the highest frequency and the lowest *f*-value while the energy of the 1L_a -band is the lowest but its *f*-value is the largest. Moreover, the 1L_a — 1L_b energy gap is smallest for this molecule. These features are similar to those observed in the isomeric cyanoanisoles and fluorobenzonitriles by Lui and McGlynn (1975a, b). Following Suzuki (1967) the higher energy of the $^1L_b \leftarrow ^1A$ transition in *p*-tolunitrile as compared to that of the *o*-isomer may be understood in

the π -state of the benzene excited states or benzene will lower the energy of the first transition of the o -molecule more than that of the p -isomer.

4.1 Estimate of π -character in the excited singlet states

To estimate the relative π -character in the first and second excited π , π^* singlet states, denoted respectively by S_1 and S_2 , of the isomeric tolunitriles, the data on the solvatochromic shifts of band origin, summarized from table 1, are presented in table 2 and analysed. The solvent-shift data in the non-polar n -hexane and MCH solvents only are considered and those in EtOH solvent are excluded because of the known complications arising with the hydrogen bonding ethanol. The shift of the positions of the origin of 1L_a - and 1L_b -band systems in going from vapour phase to the non-polar solvents may be represented by the equation,

$$\Delta\nu = \nu_{00}^{\text{gas}} - \nu_{00}^{\text{Solution}} = \left[10.71 \times \frac{10^9 f}{\nu a^3} + \frac{5031}{a^3} (\mu_e^2 - \mu_g^2) \right] \frac{n^2 - 1}{2n^2 + 1}$$

where the first term on the right side expression is the dispersion term of Bayliss (1950) and the second term represents the difference in the electrostatic energies of the excited and ground state dipolemoments embedded in a continuum of dielectric constant n^2 (Mataga and Kubota 1970). In this equation, ν and $\Delta\nu$ are in cm^{-1} , a is the cavity radius in AU, μ_e and μ_g are the dipolemoments (in Debye unit) of the excited and ground states respectively, n is the refractive index of the solvent and f represents the oscillator strength of the transition considered. From the data on the 1L_b -band of benzonitrile presented in table 2, the $\mu_e^2 - \mu_g^2$ values calculated from the above relation are $0.30 \text{ a}^3 - 0.71$ in n -hexane and $0.40 \text{ a}^3 - 0.71$ in MCH with a mean value given by $\mu_e^2 - \mu_g^2 = 0.35 \text{ a}^3 - 0.71$. Similarly for the 1L_a -band, $\mu_e^2 - \mu_g^2 = 1.36 \text{ a}^3 - 10.78$ in n -hexane and $1.43 \text{ a}^3 - 10.83$ in MCH with the average $1.40 \text{ a}^3 - 10.81$. In both the cases the $\mu_e^2 - \mu_g^2$ value computed for n -hexane and MCH solvents are about 15% of which, taking into account the uncertainties in the solvent-shift values, may be considered fairly satisfactory. The value of the dipole moment of benzonitrile in the ground state (S_0) is 4.1D (Brown 1959) and if a value of $20 \text{ \AA}^3$ is assumed for a^3 , which may not be unreasonable, the dipole moments μ_e in the $^1L_b(S_1)$ and $^1L_a(S_2)$ states work out as 4.81 and 5.83D respectively. The former may be compared with 4.45D in the first excited singlet (S_1) state estimated by Hirst and Howe (1948). These dipole moment values show that the π -character in the S_1 state is small and is moderate in the S_2 -state. It is noted that though the actual μ_e value is dependent on the assumed a^3 value nonetheless, for reasonable a^3 values μ_e in the S_2 -state is always greater than that in the S_1 -state.

The expressions for $\mu_e^2 - \mu_g^2$ relating to the $^1L_a(S_2)$ and $^1L_b(S_1)$ states of the three isomeric tolunitriles derived in the same way as in benzonitrile are shown in table 2 which also contain the μ_e -values for the two states. For p -tolunitrile the reported value of $\mu_g = 4.4 \text{ D}$ (Brown 1959) is used and for the other two molecules, for which experimental data are not available in the published literature, the respective μ_g -value has been derived by the vector-composition method. The computed values are 3.95 and 4.25 D for the o - and m -tolunitrile respectively. The μ_e -values in table 2 have been calculated with $a^3 = 25 \text{ \AA}^3$ which is a little larger than that used with benzonitrile.

for all the molecules in the S_2 state. In the S_2 state the *m*-tolunitrile molecule has more *cr*-character than the *p*-isomer which in turn seems to possess nearly the same *cr*-character as benzonitrile. The μ_e -value of *o*-tolunitrile in the S_2 -state could not be calculated because it has not been possible to determine the position of band origin owing to the broadness of its 1L_a -band even in the non-polar solvents.

4.2 Excited state molecular geometries

From the vibronic analysis of the absorption data in EtOH and MCH glasses for the three isomeric tolunitriles presented in table 3a, b and c it is seen that in all cases moderately long progressions of ring vibration frequencies are present. In *p*-tolunitrile vibronic band with five quantum of excitation of ring frequency is observed while in the *o*- and *m*-compounds respectively four and three quantum of excitations of this vibrational mode are evident. Moreover, the $\nu(\text{C-CN})$ vibrational frequency and its combination with the ring vibration frequency are also found. Similarly in the fluorescence spectra of these compounds (table 4) the ring vibration frequency seems to form the more prominent progression. These two observations are complimentary and they point to the fact that in the fluorescent S_1 -singlet state each of the tolunitrile molecules suffers small ring distortions in comparison with its geometry in the ground state (S_0). These observations and the conclusion derived therefrom is broadly the same as those made by LeBel and Laposa (1972) from the analyses of the fluorescence spectra of benzonitrile and its various deuterated derivatives. The coupling of $\nu(\text{C-CN})$ frequency probably indicates that the C-CN bond is also slightly affected in the S_1 -excited state.

The characteristics of the phosphorescence emissions of the isomeric tolunitriles in EtOH and MCH glasses have been presented in a previous section. From the vibronic data derived from these spectra, it is found that the phosphorescence spectrum of each of these molecules shows progression of a vibrational frequency (*ca.* 1600 cm^{-1}) corresponding to the $\nu(\text{C}=\text{C})$ of benzene and combinations of this frequency with ring vibration and valence $\nu(\text{C-CN})$ frequencies. These results are again similar to that reported by LeBel and Laposa (1972) from the analyses of the phosphorescence spectra of benzonitrile and the different deuterio substituted benzonitriles. Hence, their conclusion that the benzonitriles in the phosphorescence triplet state (T_1) are non-regular planar hexagons is also applicable to the tolunitriles. However, no definite suggestion about the shape of the molecules in the triplet state (T_1) could be made.

4.3 Interpretation of the variation of phosphorescence quantum yields

From the results of the present investigation it is found that the isomeric tolunitriles exhibit variations in their luminescence properties similar to those observed in isomeric cyanoanisoles and fluorobenzonitriles reported earlier (Lui and McGlynn 1975a, b). A careful examination of the data on the luminescence properties of the three substituted benzonitriles presented in table 5 reveals the following trends.

(i) The Φ_p/Φ_F -value is the highest in the para compound which also has the largest Φ_p -value. (ii) The phosphorescence lifetime (τ_p) is largest for the *m*-isomer for which

separation. (iv) The Φ_p - and τ_p -values for any member of the tolunitriles are larger than those of the corresponding member of the other two triads.

An attempt to rationalize the observed variations in the Φ_p -values of the isomers of the tolunitrile molecules has been made following the observations of Lui and McGlynn (1975a) in cyanoanisoles. For this purpose the values of intersystem crossing rate (K_{ISC}) and phosphorescence radiative rate (K_p) have been derived for the two extreme cases, in the first of which internal conversion rate (K_S) for the process $S_1 \rightarrow S_0$ is assumed to be zero and the second for which nonradiative rate (K_T) from the phosphorescent T_1 -state, i.e. $T_1 \rightarrow S_0$ is neglected as has been done by Lui and McGlynn (1975a, b). These are shown in table 5. From the K_{ISC} , K_p and Φ_p values shown in table 5 it is found that the variation of Φ_p among the isomers of any of these triads roughly follows the variations of their K_{ISC} and K_p -values calculated on either of these two assumptions.

Actually neither K_S nor K_T is entirely negligible and the choice of one of the extremes requires justification. It is seen from table 5 that for any of the tolunitriles its phosphorescence lifetime in EtOH or MCH medium is not much different from one another, which suggests that the surrounding environment does not have much influence on the nonradiative rate constant K_T and that it is essentially a molecular property. It has been found from the previous discussions that the tolunitrile molecules are slightly distorted in the first excited state (S_1) while such distortions are greater in the triplet state (T_1). Moreover, the $S_1 - S_0$ energy difference is much larger than the $T_1 - S_0$ separation. Consequently, the internal conversion rate K_S is expected to be small and the nonradiative rate K_T to be non-negligible. These arguments seem to favour the first choice for which K_S is assumed to be zero. However, this choice is not entirely satisfactory. For example, in *o*-tolunitrile though K_{ISC} and K_p are both larger than those of *p*-tolunitrile, the Φ_p of the former is less than that of the latter. This discrepancy is also seen in the cyanoanisoles but not in the fluorobenzonitriles. Most probably the steric hindrance between the substituent and the nitrile group in both *o*-tolunitrile and *o*-cyanoanisole produces the observed discrepancy.

It is also seen from table 5 that for the limit $K_S = 0$, the phosphorescence radiative rate K_p for the *m*-isomer is smaller than that for the *p*-compound in any of the triads. This is consistent with the lower Φ_p -value for the former than that of the latter. It has been shown that in the tolunitriles the π -character of the S_1 -state in the *m*- and *p*-compounds is probably the same while that in the S_2 -state it is greater in *m*- than in *p*-tolunitrile. It is known that the radiative rate (K_p) from the lowest triplet state (T_1) depends on the amount of singlet character induced in it due to coupling with the various excited singlets states and the coupling is controlled by the spin orbit matrix elements between the various excited singlets and the triplet in question. Hence the higher π -character of S_2 -state in *m*-tolunitrile would give rise to a larger spin orbit matrix in this molecule than in the para, unless the combining triplet (T_1) state in the latter has much more π -character than in the former. This conclusion is in agreement with the suggestion by Lui and McGlynn (1975a) in explaining the phosphorescence

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Spectrophotometric determination of basicities of substituted acetylbiphenyls and biphenyl carboxylic acids

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Abstract. The basicities of several 2', 3', and 4'-substituted 4-acetylbiphenyls and biphenyl-4-carboxylic acids have been determined spectrophotometrically in sulphuric acid media at 30°C. The pK_{BH^+} of 3'- and 4'-substituted compounds are correlated by the Hammett equation. The 4'-methoxy group deviates considerably in the Hammett plot. This is attributed to its conjugative interaction with the carbonyl or carboxyl group aided by protonation. Good correlation exists between pK_{BH^+} and σ^+ . The basicities of 2'-substituted 4-acetylbiphenyls and biphenyl-4-carboxylic acids reaffirm the existence of π -electron steric effect of 2'-substituents.

Keywords. Basicities; acetylbiphenyls; biphenyl carboxylic acids; Hammett equation; π -electron steric effect.

1. Introduction

The most important property of sulphuric acid-water mixtures from the point of view of their usefulness as reaction media is their acidity, measured in terms of their acidity function. The investigation of reactions in strongly acid media by Hammett (1932), Stewart and Yates (1958), Bunnett and Olsen (1965, 1966) and Arnett and Anderson (1963) has in recent years generated considerable interest. The importance of the work is brought out by Liler (1971) and Paul (1957). The measurement of the extent of protonation in these media, in conjunction with the acidity functions that the various types of bases obey, results in a large number of pK values whose correlation often leads to new insight into the analysis of the effect of structure on reactivity.

Sulphuric acid media offer an extremely wide and continuous range of acidity, joining on to the dilute aqueous range in which a large number of normally neutral compounds are protonated. The basicity of a large number of 2', 3'- and 4'-substituted 4-acetylbiphenyls and biphenyl-4-carboxylic acids was determined by the spectrophotometric technique to test the applicability of Hammett equation to the data on 3'- and 4'-substituted compounds.

2. Results and discussion

The results are given in tables 2–5. While determining the pK_{BH^+} of a base, it is important to choose the right acidity function such that pK_{BH^+} is thermodynamically

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Substituent	m.p. (°)	Formula	Observed(%)		Required(%)	
			C	H	C	H
Substituted 4-acetylbiphenyls						
H	120-121 (121) ^a	C ₁₄ H ₁₂ O	87.8	6.2	87.7	6.1
3'-F	91-92 (90.5) ^b	C ₁₄ H ₁₁ FO	78.3	5.3	78.5	5.1
3'-Cl	58-59 (57.5-58.5) ^c	C ₁₄ H ₁₁ ClO	72.8	4.9	72.7	4.8
3'-Br	45-46 (45-46) ^b	C ₁₄ H ₁₁ BrO	61.4	4.1	61.1	4.0
3'-NO ₂	110-111 (110-111) ^b	C ₁₄ H ₁₁ NO ₃	69.7	4.8	69.7	4.6
3'-CH ₃	78-79	C ₁₅ H ₁₄ O	85.8	6.8	85.7	6.7
3'-OCH ₃	89-90	C ₁₅ H ₁₄ O ₂	79.8	6.3	79.7	6.2
4'-F	105-106 (105-106) ^b	C ₁₄ H ₁₁ FO	78.6	5.3	78.5	5.1
4'-Cl	103-104 (103-104) ^b	C ₁₄ H ₁₁ ClO	72.8	4.7	72.7	4.8
4'-Br	130-131 (131) ^d	C ₁₄ H ₁₁ BrO	61.0	4.1	61.1	4.0
4'-NO ₂	153-154 (152-153) ^e	C ₁₄ H ₁₁ NO ₃	69.9	4.5	69.7	4.6
4'-CH ₃	122-123 (122) ^f	C ₁₅ H ₁₄ O	85.8	6.9	85.7	6.7
4'-OCH ₃	155-156 (153-154) ^g	C ₁₅ H ₁₄ O ₂	79.6	6.3	79.7	6.2
2'-F	85-86 (86-87) ^b	C ₁₄ H ₁₁ FO	78.4	5.3	78.5	5.1
2'-Cl	56-57 (54-56) ^b	C ₁₄ H ₁₁ ClO	72.8	4.9	72.7	4.8
2'-Br	81-82 (81-82) ^b	C ₁₄ H ₁₁ BrO	61.3	4.2	61.1	4.0
2'-NO ₂	110-111 (110) ^e	C ₁₄ H ₁₁ NO ₃	69.9	4.8	69.7	4.6
2'-CH ₃	52-53	C ₁₅ H ₁₄ O	85.6	6.8	85.7	6.7
2'-OCH ₃	63-64	C ₁₅ H ₁₄ O ₂	79.6	6.1	79.7	6.2
Substituted biphenyl-4-carboxylic acids ^d						
H	225-226 (225.8)	C ₁₃ H ₁₀ O ₂	78.9	5.3	78.8	5.1
3'-F	241-242 (240-241.5)	C ₁₃ H ₉ FO ₂	75.3	4.4	75.4	4.3
3'-Cl	248-249 (249-250)	C ₁₃ H ₉ ClO ₂	67.1	4.0	67.0	3.9
3'-Br	253-254 (252.9-254.4)	C ₁₃ H ₉ BrO ₂	56.2	3.5	56.3	3.3
3'-NO ₂	314-315 (313-315)	C ₁₃ H ₉ NO ₄	64.3	3.8	64.2	3.7
3'-CH ₃	205-206 (206-207)	C ₁₄ H ₁₂ O ₂	79.4	5.9	79.3	5.7
3'-OCH ₃	197-198 (197-198)	C ₁₄ H ₁₂ O ₃	73.9	5.7	73.7	5.3
4'-F	237-238 (236-238)	C ₁₃ H ₉ FO ₂	75.6	4.2	75.4	4.3
4'-Cl	293-294 (290-293)	C ₁₃ H ₉ ClO ₂	67.1	4.0	67.0	3.9
4'-Br	304-305 (303-305)	C ₁₃ H ₉ BrO ₂	56.1	3.5	56.3	3.3
4'-NO ₂	338-340 (336-338)	C ₁₃ H ₉ NO ₄	64.3	3.8	64.2	3.7
4'-CH ₃	242-243 (243-245)	C ₁₄ H ₁₂ O ₂	79.4	5.8	79.3	5.7
4'-OCH ₃	248-249 (247-248)	C ₁₄ H ₁₂ O ₃	73.9	5.4	73.7	5.3
2'-F	231-232 (232-233)	C ₁₃ H ₉ FO ₂	75.6	4.2	75.4	4.3
2'-Cl	251-252 (251.5-252.5)	C ₁₃ H ₉ ClO ₂	69.2	3.9	69.0	3.9
2'-Br	242-243 (242)	C ₁₃ H ₉ BrO ₂	56.5	3.4	56.3	3.3
2'-NO ₂	253-254 (253.5-254.4)	C ₁₃ H ₉ NO ₄	64.4	3.6	64.2	3.7
2'-CH ₃	205-206 (206-207)	C ₁₃ H ₁₂ O ₂	79.5	6.0	79.3	5.7
2'-OCH ₃	197-198 (197-198)	C ₁₄ H ₁₂ O ₃	74.0	5.6	73.7	5.3

Values in parentheses are literature values

^a Long and Henze (1941); ^b Byron *et al* (1966); ^c Inukai (1962); ^d Carpenter and Turner (1934); ^e Grieve and Hey (1932-1934); ^f NgPh *et al* (1951); ^g Ray and Rieveschl (1965)

significant. In order to test this, log *I* is plotted against the H₀ acidity function so that the slope of the straight line is minus unity. The pK_{BH⁺} values show a regular variation with substituents: electron-withdrawing groups decrease and electron-donating groups

Table 2. pK_{BH^+} of substituted biphenyl-4-carboxylic acids obtained from the plot $\log I$ vs H_0

Substituent	r	$-c$	$-m$	c/m	$-pK_{BH^+}$
H	0.999	6.85	0.951	6.90	6.9
3'-F	0.999	6.68	0.952	7.02	7.0
3'-Cl	0.999	6.72	0.949	7.08	7.1
3'-Br	0.995	6.74	0.951	7.09	7.7
3'-NO ₂	0.999	6.85	0.945	7.25	7.2
3'-CH ₃	0.990	6.50	0.949	6.85	6.9
3'-OCH ₃	0.994	6.66	0.949	7.00	7.0
4'-F	0.999	6.59	0.951	6.93	6.9
4'-Cl	0.990	6.66	0.951	7.00	7.0
4'-Br	0.999	6.68	0.952	7.02	7.0
4'-NO ₂	0.998	6.97	0.947	7.36	7.4
4'-CH ₃	0.999	6.46	0.950	6.80	6.8
4'-OCH ₃	0.990	6.15	0.954	6.45	6.4
2'-F	0.999	6.51	0.949	6.86	6.9
2'-Cl	0.999	6.46	0.946	6.82	6.8
2'-Br	0.990	6.43	0.946	6.80	6.8
2'-NO ₂	0.999	6.49	0.952	7.03	7.0
2'-Me	0.998	6.36	0.952	6.68	6.7
2'-OMe	0.990	6.20	0.953	6.51	6.5

pK_{BH^+} values are accurate within ± 0.2 unit; r = correlation coefficient; m = slope in the plot of $\log I$ vs H_0 ; c = intercept in the plot of $\log I$ vs H_0

Table 3. pK_{BH^+} of substituted biphenyl-4-carboxylic acids obtained by Bunnett-Olsen treatment.

Substituent	r	[H ₂ SO ₄] at half-protonation		$-pK_{BH^+}$
		ϕ	% (w/w)	
H	0.999	0.053	79.33	6.9
3'-F	0.995	0.052	80.15	6.8
3'-Cl	0.999	0.075	80.56	6.8
3'-Br	0.988	0.067	80.64	6.8
3'-NO ₂	0.976	0.079	81.78	6.9
3'-CH ₃	0.998	0.045	78.92	6.6
3'-OMe	0.998	0.052	80.07	6.7
4'-F	0.969	0.058	79.74	6.7
4'-Cl	0.997	0.074	80.15	6.7
4'-Br	0.983	0.065	80.15	6.8
4'-NO ₂	0.982	0.079	82.52	7.1
4'-CH ₃	0.993	0.031	78.59	6.5
4'-OMe	0.978	0.041	75.57	6.2
2'-F	0.999	0.053	78.84	6.6
2'-Cl	0.997	0.042	78.27	6.5
2'-Br	0.987	0.028	78.27	6.5
2'-NO ₂	0.998	0.064	80.07	6.7

Table 4. pK_{BH^+} of substituted 4-acetylbiphenyl obtained from $\log I$ vs H_0 plot.

Substituent	r	$-c$	$-m$	c/m	$-\text{pK}_{\text{BH}^+}$
H	0.995	5.69	0.909	6.25	6.3
3'-F	0.990	6.08	0.938	6.48	6.5
3'-Cl	0.999	6.12	0.941	6.50	6.5
3'-Br	0.995	6.19	0.953	6.50	6.5
3'-NO ₂	0.999	6.29	0.933	6.74	6.8
3'-Me	0.999	5.85	0.967	6.05	6.0
3'-OMe	0.990	6.10	0.960	6.35	6.4
4'-F	0.999	5.90	0.936	6.30	6.2
4'-Cl	0.998	5.95	0.930	6.39	6.4
4'-Br	0.990	6.01	0.940	6.39	6.4
4'-NO ₂	0.999	6.36	0.926	6.87	6.9
4'-Me	0.990	5.84	0.974	6.00	6.0
4'-OMe	0.995	5.42	0.984	5.51	5.5
2'-F	0.999	5.69	0.931	6.11	6.1
2'-Cl	0.999	5.68	0.937	6.08	6.1
2'-Br	0.999	5.66	0.933	6.07	6.1
2'-NO ₂	0.990	6.20	0.949	6.53	6.5
2'-Me	0.999	5.52	0.936	5.90	5.9
2'-OMe	0.999	5.47	0.974	5.6	5.6

pK_{BH^+} values are accurate within ± 0.2 unit

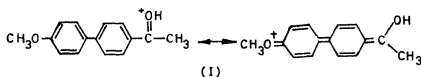
Table 5. pK_{BH^+} of substituted 4'-acetylbiphenyls by Bunnett-Olsen treatment.

Substituent	r	[H ₂ SO ₄] at half protonation		$-\text{pK}_{\text{BH}^+}$
		ϕ	% (w/w)	
H	0.989	0.096	74.0	5.8
3'-F	0.969	0.067	75.7	6.1
3'-Cl	0.993	0.064	76.1	6.1
3'-Br	0.983	0.048	76.1	6.2
3'-NO ₂	0.998	0.073	78.1	6.4
3'-Me	0.960	0.036	72.3	5.7
3'-OMe	0.996	0.043	74.8	6.0
4'-Fe	0.953	0.081	74.3	5.8
4'-Cl	0.997	0.076	75.2	6.0
4'-Br	0.955	0.064	75.2	6.0
4'-NO ₂	0.970	0.083	79.0	6.5
4'-Me	0.992	0.028	71.9	5.6
4'-OMe	0.999	0.017	68.0	5.2
2'-F	0.997	0.073	72.9	5.7
2'-Cl	0.890	0.065	72.5	5.7
2'-Br	0.909	0.060	72.5	5.7
2'-NO ₂	0.965	0.043	76.2	6.3

Substituent	By FMMF method	From pKa values
3'-F	0.107	0.146
3'-Cl	0.122	0.146
3'-Br	0.130	0.115
3'-NO ₂	0.255	0.162
3'-CH ₃	-0.030	-0.054
3'-OCH ₃	0.022	-0.031
4'-F	0.044	0.085
4'-Cl	0.093	0.154
4'-Br	0.102	0.154
4'-NO ₂	0.308	0.323
4'-CH ₃	-0.065	-0.039
4'-OCH ₃	-0.084	-0.108

values by dividing the Δ pKa values by a ρ value of 1.32 based on benzoic acid ionization in 50% 2-*n*-butoxyethanol-water. The new σ values thus calculated are given in table 6. The Hammett correlations with these values were very poor, the 4'-OMe group deviating considerably. Neglecting this group the correlation produces $r = 0.871$ and $s = 0.127$ in ketones and $r = 0.812$ and $s = 0.110$ in acids. The poor correlation possibly lies in the pKa values of Byron *et al* (1966) which generated separate lines for 3'- and 4'-substituted biphenyl-4-carboxylic acids when plotted against ordinary σ values. When the pK_{BH^+} values are plotted (figure 1) against ordinary Hammett σ_m and σ_p values respectively for 3'- and 4'-substituents the correlation seems to be much better without 4'-OMe, with $r = 0.958$ and $s = 0.052$ in ketones and $r = 0.954$ and $s = 0.041$ in acids. However, the correlation with σ_{ij} values calculated (table 6) based on the Dewar-Golden-Harris treatment (1971) was satisfactory for all the groups except 4'-OMe with $r = 0.971$ and $s = 0.062$ for ketones and $r = 0.968$ and $s = 0.045$ for the acids. This provides an interesting confirmation that the DGH treatment is fairly successful for biphenyl (figure 2).

Being an electron-donating group, 4'-OMe is involved in extended conjugation with the protonated carbonyl or carboxyl groups as illustrated in (I).



This type of direct resonance may be responsible for the departure of the group from the Hammett plot. When σ^+ constants of Brown and Okamoto (1958) are used in place of σ_m and σ_p , the correlation is excellent, the 4'-OMe group also falls on the line (figure 3). The correlation coefficient is 0.977 with $s = 0.053$ for ketones and 0.965 with $s = 0.062$ for acids. The plot of nK_{BH^+} vs pKa of the 2'-substituted biphenyl-4-

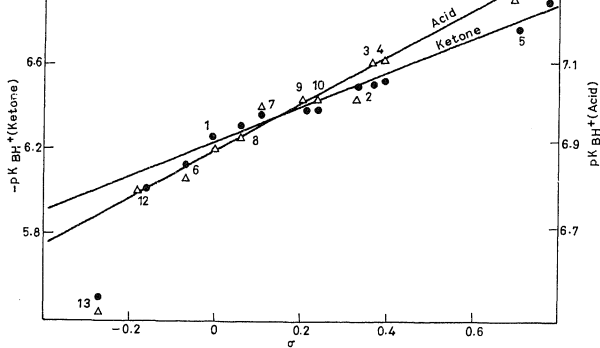


Figure 1. pK_{BH^+} vs Hammett σ plot.

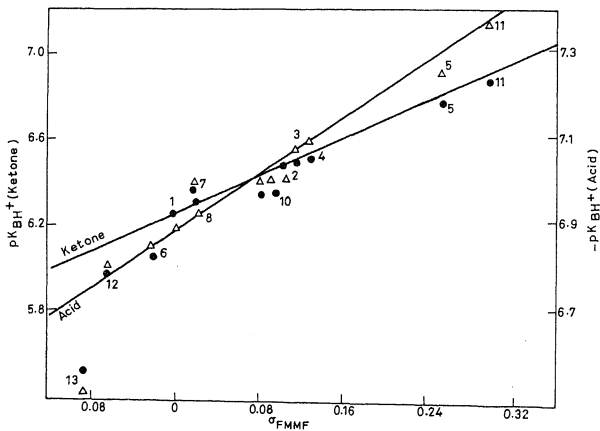


Figure 2. pK_{BH^+} vs σ_{FMMF} plot.

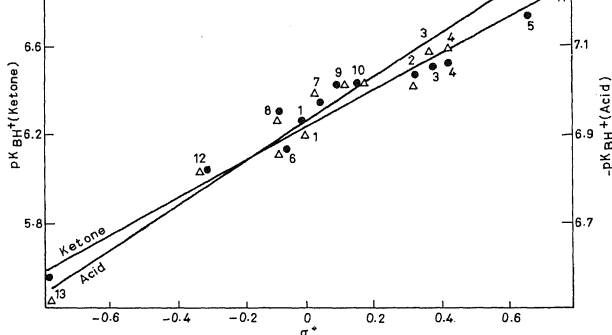


Figure 3. pK_{BH^+} vs σ^+ plot.

3. Experimental

3.1 Preparation of compounds

All the ketones were prepared as described by Byron *et al* (1966) and the acids obtained by hypochlorite oxidation. The purity of the compounds tested by TLC gave good carbon and hydrogen analyses (table 1).

3.2 Measurement of pK_{BH^+}

Sulphuric acid (E Merck, AR) was diluted with water and 50–98 % (w/w) solutions were prepared. pK_{BH^+} was determined by the procedure adopted by Ananthakrishna Nadar and Varghesetharumaraj (1981). A weighed sample of each compound was dissolved in 85 % (w/w) sulphuric acid-water to give a 4×10^{-4} M stock solution, from which 1 ml aliquots was pipetted out into 10 ml volumetric flasks and made up to mark with suitable sulphuric acid-water mixtures so as to give solutions of desired acid concentrations. The H_0 values were taken from the compilation of Paul and Long (1957). Trial experiments indicated that all the ketones and acids were almost unprotonated up to 50 % sulphuric acid solution and almost completely protonated in 95 % and above sulphuric acid solution. The uv absorption spectra of the compounds were recorded in 50 and 95 % sulphuric acid solutions, to obtain the wavelengths of maximal absorption of the unprotonated (λ_B) and of the protonated (λ_{BH^+}) forms. The λ values did not change with change in medium. The extinction coefficients in all the other solutions were determined at these two wavelengths.

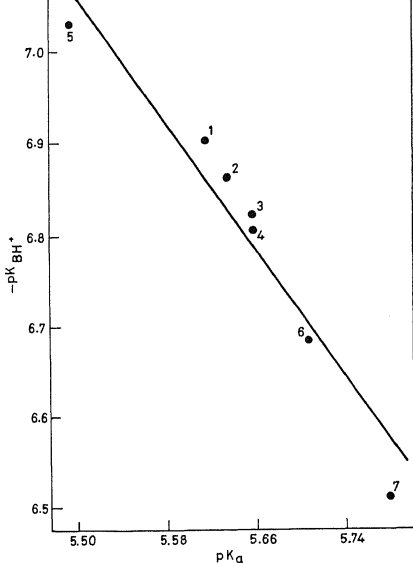


Figure 4. pK_{BH^+} vs pK_a plot for 2'-substituents.

The ionization ratio I in each solution was determined as follows:

$$I = (\varepsilon - \varepsilon_B) / (\varepsilon_{BH^+} - \varepsilon) \quad (1)$$

where ε is the molar extinction coefficient in the chosen acid solution, ε_{BH^+} and ε_B are the corresponding values of the completely protonated and the unprotonated forms respectively. The ionization ratio is related to H_0 through

$$\log I = mH_0 + C. \quad (2)$$

From the plot of $\log I$ vs H_0 , the H_0 value at half protonation ($H_0^{1/2}$) is taken as pK_{BH^+} . Following the treatment of Bunnett and Olsen (1965), the pK_{BH^+} values are also determined graphically employing equation (3)

$$\log [BH^+] / [B] + H_0 = \phi(H_0 + \log CH^+) + pK_{BH^+} \quad (3)$$

The intercept in the plot between $\log [BH^+] / [B] + H_0$ and $(H_0 + \log CH^+)$ gives

obtained by equation (3) and hence the values obtained from equation (2) are used in the correlation.

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Effect of substituents on the oxidation of some alkyl-aryl sulfoxides by chloramine-T

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Abstract. The oxidation rates of some substituted phenyl methyl sulfoxides with chloramine-T have been studied in alkaline and neutral media. OsO_4 is used as catalyst in alkaline medium where the meta and para substituents show no effect on the reaction rate. This is explained on the basis of isokinetic relationship. In both the media, the orthosubstituents show steric effect.

Keywords. Chloramine-T; isokinetic; kinetics; steric effect; sulfoxides.

1. Introduction

The kinetics of oxidation of some substituted phenyl methyl sulfoxides by CAT in alkaline medium (Ganapathy and Jayagandhi 1982a) and in buffered ethanol-water (Ganapathy and Jayagandhi 1982b) have been studied. In this paper, the substituent effects are analysed in terms of steric factor and isokinetic relationship.

2. Experimental

Chloramine-T and the sulfoxides were prepared and purified using standard methods. Alkaline medium was maintained using NaOH. *t*-Butanol-water mixture (1 : 1 v/v) was used as solvent. For the buffered medium, phosphate buffer (pH 7) was used and ethanol-water mixture (1 : 1 v/v) was used as solvent. Both the kinetics were followed iodometrically.

3. Results and discussion

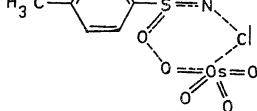
3.1 Alkaline medium

The observed rate-law for the Os(VIII)-catalysed oxidation of substituted phenyl methyl sulfoxides by CAT (Ganapathy *et al* 1982a) is

$$-d[\text{CAT}]/dt = k_{1.5}[\text{CAT}][\text{SO}]^{1/2}.$$

The mechanism is proposed by assuming the formation of the following cyclic complex between CAT and OsO_4 .

The cyclic structure indicates that the electron density around nitrogen is decreased



in complexation, weakening the N-Cl bond. Therefore, the interaction with the sulfoxides is increased resulting in the formation of chlorosulphonium ion intermediates. This, on hydrolysis, gives the sulphone.

The calculated rate constants and the activation parameters for the meta and para substituted phenyl methyl sulfoxides are given in tables 1 and 2 respectively.

A perusal of the rate data indicate that there is no substituent effect on the reaction rate. This may be due to two factors (i) a zero-order dependence on the substrate and (ii) the experimental temperature being too close to the isokinetic temperature (Leffler 1955; Leffler and Grumwald 1963; Peterson *et al* 1961). The first probability is ruled out as the present reaction showed a clear dependence (0.5) on the substrate. Hence, the only probability is that the experimental temperature should be in the neighbourhood of isokinetic temperature.

A plot of $\Delta H^\ddagger$ vs $\Delta S^\ddagger$ gives an excellent straight line with a correlation coefficient (r) of 1. The isokinetic temperature obtained from the slope is 305°K. It is probable that at the experimental temperatures employed (298, 303 and 308°K) there will be equilibration of the rates.

The free energy of activation $\Delta G^\ddagger$ is equal to $(\Delta H^\ddagger - T\Delta S^\ddagger)$ and it follows that if there is an exact linear relationship between $T\Delta S^\ddagger$ and $\Delta H^\ddagger$, with unit slope, there will be no variation in $\Delta G^\ddagger$ i.e. all the rate constants are equal. The present reaction series showed an excellent relationship between $T\Delta S^\ddagger$ and $\Delta H^\ddagger$ with a correlation coefficient of 0.998. The slope of the line was 0.984 (nearly unity) which clearly explains that there

Table 1. Rate constants for Os(VIII)-catalysed oxidation of meta and para substituted phenyl methyl sulfoxides by chloromine-T.
[NaOH] = 0.002 M; [OsO₄] = 0.0002 M

Substituent	$k_{1-5} \times 10^3 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ sec}^{-1}$		
	25°	30°	35°
None	4.612	5.850	7.086
<i>p</i> -OCH ₃	4.990	5.975	7.372
<i>p</i> -Cl	4.557	5.727	6.551
<i>p</i> -Br	4.756	5.982	7.224
<i>p</i> -CH ₃	4.662	5.968	7.503
<i>p</i> -NO ₂	4.907	6.085	7.835
<i>m</i> -OCH ₃	4.618	5.967	7.232
<i>m</i> -Cl	4.637	5.778	7.290
<i>m</i> -CH ₃	4.180	5.583	7.120

Substituent	E (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹ at 30°)	$\Delta S^\ddagger$ (kJ ⁻¹ mol ⁻¹ at 30°)	$\Delta G^\ddagger$ (kJ mol ⁻¹ at 30°)
None	33.77	31.25	-185.2	87.36
<i>p</i> -OCH ₃	29.16	26.64	-200.2	87.31
<i>p</i> -Cl	28.71	26.19	-201.5	87.25
<i>p</i> -Br	32.48	29.96	-189.3	87.31
<i>p</i> -CH ₃	35.78	33.26	-178.4	87.31
<i>p</i> -NO ₂	36.54	34.02	-175.7	87.26
<i>m</i> -OCH ₃	32.81	30.20	-188.2	87.31
<i>m</i> -Cl	33.77	31.25	-185.3	87.40
<i>m</i> -CH ₃	42.83	40.31	-155.7	87.48
<i>m</i> -NO ₂	28.71	26.19	-201.5	87.25

Table 3. Rate constants for Os(VIII)-catalysed oxidation of ortho-substituted phenyl methyl sulfoxides with chloramine-T.

[NaOH] = 0.002 M; [OsO₄] = 0.0002 M

Substituent	$k_{1,5} \times 10^3 \text{ l}^{1/2} \text{ mol}^{-1/2} \text{ sec}^{-1}$		
	25°	30°	35°
None	4.612	5.850	7.086
Cl	1.697	2.041	2.516
Br	1.676	2.093	2.771
OCH ₃	2.146	2.652	3.359
CH ₃	1.915	2.334	3.140
NO ₂	2.441	3.079	3.845
2,6-(CH ₃) ₂	0.796	1.134	1.642

is exact compensation between $T\Delta S^\ddagger$ and $\Delta H^\ddagger$.

The rate constants and the thermodynamic parameters for the orthosubstituted phenyl methyl sulfoxides are given in tables 3 and 4 respectively. Leffler (1955) pointed out that moderate changes in the degree of steric hindrance often do not remove a reaction from its isokinetic line but merely move it to a new location on the same line. With a considerable increase in steric hindrance in the transition state, a combined increase in the enthalpy of activation and decrease in entropy of activation are to be expected. Such points lie above the isokinetic line for the other reactions. In this study the points corresponding to the orthosubstituted sulfoxides lie above the isokinetic line showing steric effect (figure 1).

2.2 Neutral medium

The rate-law used to calculate the rate constants k_1 and k'_2 is

$$\text{rate}/[C][SO] = k_1 + k'_2 [C]/[SA]$$

Substituent	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (kJ mol ⁻¹) at 30°)	$\Delta S^\ddagger$ (kJ mol ⁻¹) at 30°)	$\Delta S^\ddagger$ (kJ mol ⁻¹) at 30°)
None	33.77	31.25	-185.2	87.36
Cl	30.83	28.31	-203.7	90.02
Br	39.55	37.03	-174.7	89.95
OCH ₃	33.49	30.97	-192.7	89.36
CH ₃	37.21	34.69	-181.5	89.68
NO ₂	34.17	31.65	-189.2	88.98
2,6-(CH ₃) ₂	57.41	54.89	-120.8	91.50

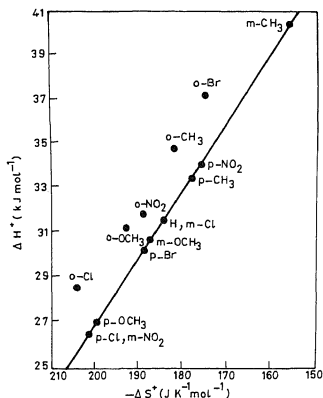


Figure 1. Plot of $\Delta H^\ddagger$ vs $\Delta S^\ddagger$ for the reaction of chloramine-T with substituted phenyl methyl sulfoxides in alkaline medium.

where $[SA]$ is the concentration of *p*-toluenesulphonamide formed during the reaction. k_1 and k_2 are the rate constants for the reaction of $RNHCl$ and $RNCl_2$ with the sulfoxides, respectively. The rate constants k_1 and k'_2 are given in tables 5 and 6 respectively.

The rate constants of ortho-substituted phenyl methyl sulfoxides clearly reveal that the rates are very much lower than those obtained for the corresponding meta and para substituted sulfoxides. The steric effect of an ortho-substituent can be estimated by calculating the ratio of the rate constants of the ortho and para substituted sulfoxides (Capon 1964). The very small relative rate values for methyl and chloro substituents

Substituent	$k_1 \times 10^4 \text{ l mol}^{-1} \text{ sec}^{-1}$		
	35°	40°	45°
None	46.67	67.68	104.20
OCH ₃	48.32 (0.463)	53.45 (0.371)	61.70 (0.322)
CH ₃	9.26 (0.075)	10.50 (0.066)	11.78 (0.068)
Cl	1.13 (0.069)	1.59 (0.077)	3.43 (0.131)
Br } NO ₂ }	The reactions are too slow for measurement		

The $k_1(o)/k_1(p)$ values are given within brackets.

Table 6. Rate constants for the reaction of RNCl_2 with ortho-substituted phenyl methyl sulfoxides.

Substituent	$k'_2 \times 10^5 \text{ l mol}^{-1} \text{ sec}^{-1}$		
	35°	40°	45°
None	1678	2069	2265
OCH ₃	1001 (0.394)	1095 (0.349)	1246 (0.323)
CH ₃	310.8 (0.128)	412.0 (0.120)	486.3 (0.122)
Cl	4.82 (0.012)	6.02 (0.013)	8.95 (0.015)
Br } NO ₂ }	The reactions are too slow for measurement		

The $k'_2(o)/k'_2(p)$ values are given within brackets.

show the steric effect. The reactions of CAT with nitro and bromo substituted sulfoxides are too slow for measurement. This may be due to the lower stability of the transition state because there is greater crowding in the transition state.

Among the ortho-substituted phenyl methyl sulfoxides, the highest rate was observed for *o*-methoxyphenyl methyl sulfoxide, whose rate constant (k_1) is higher than that for methyl phenyl sulfoxide. Such a high rate deserves special attention in view of the neighbouring group effect on the *o*-OCH₃ group. The presence of an ortho-substituent (in this case the reaction centre itself) restricts the free rotation of the methoxy group and increases its probability of attaining planarity with the benzene ring. Thus there can be enhanced conjugation of the methoxy group with the reaction centre. This may explain the higher rate observed for *o*-methoxyphenyl methyl

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Spectroscopic studies of the electron donor-acceptor interactions of aromatic hydrocarbons with tetrachlorophthalic anhydride

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Abstract. Electron donor-acceptor (EDA) interactions of tetrachlorophthalic anhydride (TCPA) with benzene, *p*-xylene, mesitylene, fluorene, *t*-stilbene and pyrene have been investigated by spectroscopic technique. The spectroscopic and thermodynamic parameters of the complexes formed are reported. The enthalpies of formation range between 0.2 to 5.0 kcal mole⁻¹. Among all the donors studied, pyrene appears to be the strongest electron donor towards tetrachlorophthalic anhydride.

Keywords. Tetrachlorophthalic anhydride; electron donor acceptor complexes; formation constants; spectroscopic studies.

1. Introduction

Our interest in tetrachlorophthalic anhydride (TCPA) as electron acceptor arose from the observation that the electron affinity of TCPA (1.8 eV) is comparable to that of 1,3,5-trinitrobenzene (1.86 eV), which is known to be a good electron acceptor. In spite of this, relatively little attention has been focussed towards investigating the electron donor-acceptor (EDA) complexes of TCPA (Dwivedi and Banga 1980a). Stable molecular complexes of TCPA with aromatic hydrocarbons and aza-aromatics are known (Czekalla 1956) to form. Formation constants of 1:1 EDA complexes of polynuclear aromatic hydrocarbons with TCPA have been determined by Chowdhury and Basu (1960). Dwivedi and Banga (1980a) have reported the enthalpies of formation of a number of EDA complexes formed between aromatic hydrocarbons and TCPA. The $h\nu_{CT}$ -ionization potential plot was found to be linear. As part of an extended programme to study the EDA complexes of TCPA, we have presently investigated the interaction of TCPA with benzene, *p*-xylene, mesitylene, fluorene, *t*-stilbene and pyrene.

2. Experimental

Benzene, *p*-xylene (BDH, AR) and mesitylene (SRL) were purified by fractional distillation. Fluorene, *t*-stilbene and pyrene (supplied by Aldrich Chemical Co., USA) were purified by recrystallization from alcohol. TCPA was repeatedly crystallized from benzene until its absorption spectrum in CCl₄ showed no further change on successive crystallization. CCl₄ (E. Merck, G. R.) was dried and distilled before use.

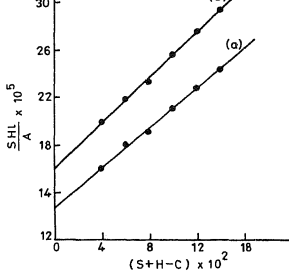


Figure 1. Modified Scott equation plot for the fluorene-TCPA complex at **a.** 21°C and **b.** 31°C. (*S* and *H* are the initial concentrations of the donor and acceptor, *C* is the concentration and *A* is the absorbance of the complex and *l* is the optical path length).

fitted with variable temperature cell compartment using matched silica cells of 1 cm path length. Equilibrium constant of formation, *K*, and molar extinction coefficient, ϵ , of the EDA complexes were determined employing the modified Scott equation (Scott 1956) by measuring the absorbance (at the λ_{max} of the charge-transfer band) of a series of solutions with varying donor concentration and a fixed TCPA concentration. In evaluating *K*, Person's criteria regarding donor concentration were satisfied (Person 1965). The *K* and ϵ values of the complexes have an uncertainty of less than $\pm 10\%$ as can be seen from figure 1 for the Fluorene-TCPA system. The enthalpies of formation, ΔH , of the EDA complexes were evaluated from the equilibrium constants at different temperatures in the range 10–40°C. Freshly prepared stock solutions of the donor and acceptor were used in all the measurements.

3. Results and discussion

The charge-transfer bands of all the EDA complexes appear in the region of the donor absorption and therefore the charge-transfer band maxima (λ_{CT} values) were obtained by difference spectra (figure 2). The results of the present investigation are summarised in table 1. The λ_{CT} values for the EDA complexes of TCPA with *t*-stilbene and pyrene agree well with those reported by Chowdhury and Basu (1960). However, the *K* and ϵ values in these systems differ from our data. We believe that the present values are more reliable since the donor concentration employed was sufficiently high and satisfied Person's (1965) criteria. Mulliken (1952) pointed out that the lower the ionization potential, higher will be the stability (as measured by *K* and ΔH) of the EDA complex. This is found to be true from our data in table 1. While uncertainties in the determination of ΔH in systems with small *K* values would be large, the ΔH values are estimated to be well within $\pm 10\%$ even after accounting for all possible sources of error. These ΔH and *K* values for the complexes studied are comparable to other π -donor- π -acceptor systems (Rao *et al* 1971), indicating that TCPA acts as a π -acceptor in

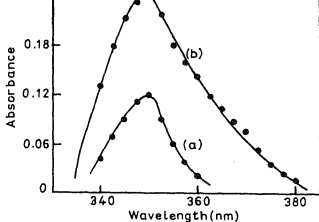


Figure 2. Electronic absorption spectra of **a.** benzene (0.4 M) + TCPA (4.0×10^{-4} M) and **b.** *p*-xylene (0.4 M) + TCPA (4.0×10^{-4} M) in CCl_4 solution.

Table 1. Spectroscopic and thermodynamic data for EDA complexes of aromatic hydrocarbons with TCPA in CCl_4 solution.

Donor	I_p (eV)	λ_{CT} (nm)	K^* (l mol^{-1})	ϵ ($\text{l mol}^{-1} \text{cm}^{-1}$)	$-\Delta H$ (k cal mol^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	f
mesitylene	9.24	350	1.5 ± 0.1	666 ± 40	0.24 ± 0.02	1243	0.003
fluorene	8.44	350	2.2 ± 0.2	1363 ± 40	0.46 ± 0.03	1787	0.011
<i>p</i> -xylene	8.39	350	3.5 ± 0.2	1500 ± 50	1.6 ± 0.1	2152	0.014
benzene	—	350	6.7 ± 0.2	1177 ± 50	2.6 ± 0.2	812	0.004
pyrene	7.99	350	7.7 ± 0.1	1077 ± 40	3.6 ± 0.2	1124	0.005
anthracene	7.82	425	10.4 ± 0.1	1300 ± 50	5.0 ± 0.2	3323	0.043

21°; data are given at one temperature only for the sake of brevity.

$\Delta\nu_{1/2}$, ϵ and oscillator strength (f) data can be analysed if one carefully chooses donor molecules which are similar in structure. Thus, if the donors in table 1 are divided into three separate groups of methyl substituted (group 1), phenyl substituted (group 2) and polynuclear hydrocarbons (group 3), the $\Delta\nu_{1/2}$ order is:

mesitylene > *p*-xylene > benzene

t-stilbene < benzene

pyrene > fluorene < benzene

The $\Delta\nu_{1/2}$ values increase with increasing complex strength (as measured by $-\Delta H$) with the exception of benzene. This direct relationship between $\Delta\nu_{1/2}$ and the strength of the complexes was observed earlier (Dwivedi and Banga 1980b; Dwivedi *et al* 1982) and was attributed to the large resonance interaction in the complexes.

The ϵ and f values of the EDA complexes provide a measure of the intensity of the charge-transfer (CT) band. Based on these data in table 1, the CT band intensity order is:

mesitylene > *p*-xylene > benzene

It is, thus, seen that the intensity of the π band increases as the strength of interaction increases in electron donors of all the three groups. This observation is similar to that reported by Daisey and Sonnessa (1972) and Dwivedi and Banga (1980b,c) for number of EDA complexes.

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A zero differential overlap study of chemical binding in ammonia-borane and carbonyl-borane

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Abstract. A CNDO/2D study of the charge distribution obtained through Mulliken population analysis in the ground state of the title compounds shows that the features of charge distribution found by several *ab initio* calculations are fairly well reproduced by this method. The one-particle density, the interference density at the mid-point of the bond axis and the kinetic part of the interference energy calculated through the deorthogonalized density matrices over a wide range of intermolecular separation between the donor and the acceptor show that the one-particle density and the interference density steadily grow with decreasing internuclear separation, while the kinetic interference energy starts with negative value at large distance, then decreases and passes through a minima near but above the equilibrium distance and then increases rapidly below it conforming to the characteristic general behaviour of the kinetic component of Morse curve. The orbital pairwise interference density and the corresponding kinetic energy components reveal that the orbitals involved in the covalent binding are σ_{2p} AO of B and 2S and σ_{2p} AO of N and C atoms in $\text{H}_3\text{B}-\text{NH}_3$ and $\text{H}_3\text{B}-\text{CO}$ respectively.

Keywords. ZDO; deorthogonalization; one-particle density; interference density; kinetic interference energy; ammonia-borane; carbonyl-borane.

1. Introduction

According to the conventional concept of chemists, ammonia borane (or borazane), $\text{H}_3\text{B}-\text{NH}_3$, and carbonyl borane, $\text{H}_3\text{B}-\text{CO}$, are formed by the sharing of a lone pair of electrons belonging to the donor groups (NH_3 , CO) with the vacant orbital of the acceptor group (BH_3). The newly formed B-L bond (L is any ligand) is of pivotal importance to account for the stability and characteristics of such boron coordination compounds. A number of theoretical calculations probing the various aspects of these two molecules have appeared (Das 1957; Hoffmann 1964; Veillard *et al* 1967; Moireau and Veillard 1968; Peyerim Hoff and Buenker 1968; Armstrong and Perkins 1969; Lloyd and Lynaugh 1970, 1972; Frost 1970; Shillady *et al* 1971; Gordon and England 1972; Palke 1972; Bach *et al* 1973; Fujimoto *et al* 1974; Kato *et al* 1974; Purcell and Martin 1974; Runtz and Bader 1975; Dill *et al* 1975; Umeyama and Morokuma 1976; Ermler *et al* 1976; Ha 1976; Datta *et al* 1977; Redmon *et al* 1979; Zirz and Alrichs 1981).

The probing into the nature of the newly formed bond of these compounds has so far been in terms of Mulliken (1955) population analysis which can make only a qualitative prediction as to the distribution of electrons and the binding effect. Ruedenberg (1962) suggested an energy analysis, based on density matrix properties, which can extract significant energetic information that provides a quantitative basis of reasoning about the contributory factors to chemical binding. Ruedenberg concluded that the

kinetic energy, and this has kinetic energy due to interference. The concept was applied to a number of molecular system (Layton Jr and Ruedenberg 1964; Rue and Ruedenberg 1964; Edmiston and Ruedenberg 1964; Popkie and Moffatt 1968; Fienberg *et al* 1970). Wilson and Goddard (1970, 1972) critically analyzed the role of kinetic energy in covalent binding and concluded, from the analysis of GI functions of molecules, that lowering of a non-classical 'exchange kinetic energy' is responsible for chemical binding and this 'exchange kinetic energy' is related to the interference kinetic energy of Ruedenberg. Recently, a number of reports have appeared on the calculation of interference density and the kinetic interference energy (Datta 1976; Datta and Datta 1978), but some fundamental discrepancies are evident in this work (*vide infra*).

The purpose of the present investigation is to extract information as to whether Ruedenberg's type of binding analysis can be attempted by semi-empirical ZDO methods like CNDO/2 (Pople *et al* 1965). The CNDO/2 method, inspite of its success in correlating a number of molecular properties with experimental results (Pople and Gordon 1967) and its easy applicability to large molecules, especially, the boron coordination compounds (Labarre 1978), calculates unrealistic charge distribution (Shillady *et al* 1971) because, the basis functions of this formalism are virtually a set of orthogonalized AO's (Pople and Segal 1965).

The spinless one-particle (electron) density $\rho(R)$ at a position R for a closed shell molecular system expanded in terms of AO's takes the form

$$\rho(R) = \sum_{r,s} P(r,s) \phi_r(R) \phi_s(R), \quad (1)$$

where $P(r,s)$ are the elements of bond order matrix and ϕ_i 's are the basis set. Integration of $\rho(R)$, over all space, for methods that include overlap, gives the population breakdown

$$N = \int \rho(R) dR = \sum_{r,s} P(r,s) S(r,s) \quad (2)$$

$$= \sum_A^{\text{atoms}} P_A^N + \sum_A^{\text{atoms}} \sum_{B>A}^{\text{atoms}} P_{AB}, \quad (3)$$

where N is the total number of electrons and $S(r,s)$ is the overlap integral between AO's r and s , and P_A^N and P_{AB} are the net atomic and overlap populations respectively,

$$P_A^N = \sum_r^A \sum_s^A P(r,s) S(r,s), \quad (4)$$

$$P_{AB} = 2 \sum_r^A \sum_s^B P(r,s) S(r,s), \quad (5)$$

but for ZDO methods, (2) takes the form

$$N = \sum_A^{\text{atoms}} \sum_r^A P(r,r). \quad (6)$$

Ruedenberg suggested a partitioning of the electron density $\rho(R)$ into the quasi-classical density $\rho^{\text{cl}}(R)$ and interference density $\rho^{\text{I}}(R)$

$$N = \int \rho(R) dR = \int \rho^{cl}(R) dR, \quad (8)$$

$$\int \rho'(R) dR = 0. \quad (9)$$

Using the conditions (8) and (9), and applying the series of approximation regarding interacting orbital pair (Ruedenberg 1962; Edmiston and Ruedenberg 1964) the formula of interference density has been derived as

$$\rho' = \sum_{Aa, Bb} \rho'(Aa Bb) = \sum_{Aa, Bb} P(Aa Bb) \langle Aa Bb \rangle, \quad (10)$$

where Aa, Bb are AO's centred on atoms A and B respectively, $P(Aa Bb)$ is the element of the overlap matrix and $\langle Aa Bb \rangle$ is the orbital interference density for the orbital pair (Aa, Bb)

$$\langle Aa Bb \rangle = Aa \cdot Bb - \frac{1}{2} S(Aa Bb) (Aa^2 + Bb^2), \quad (11)$$

where $S(Aa Bb)$ is the overlap integral of the AO pair. To measure the degree to which the orbital pair (Aa) is effective in creating interference effect, Ruedenberg, similar to that of Pritchard (1951) and Mulliken (1955), partitioned the population $q(Aa)$ of the orbital pair into 'valence inactive', $P(Aa)$, and 'valence active', $v(Aa)$, parts.

$$q(Aa) = P(Aa) + v(Aa), \quad (12)$$

and,

$$P(Aa) = P(Aa Aa), \quad (13)$$

$$v(Aa) = \sum_{Bb} P(Aa Bb) S(Aa Bb). \quad (14)$$

The relative size and sign of $v(Aa)$ determines the binding capacity of the orbital (Aa) . Now under a ZDO formalism, the overlap distribution $(Aa \cdot Bb)$ and the overlap integral $S(Aa Bb)$ are all zero thereby excluding any possibility of inclusion of interference effect in CNDO/2 method, and the electron density is given by the quasielectronic density only and the valence activity (equation (14)) is zero. For the same reason, overlap population, although used as bond index (Fischer and Kollmar 1970; Pritchard and Seltzer 1971; Corre 1981), cannot be extracted from a CNDO/2 calculation because the total charge density is divided out formally among the atoms alone (equation 6), and under such a formalism, the identification of bond is not straightforward (McIver *et al* 1971; Driessler and Kutzelnigg 1977).

Thus it is apparent that the CNDO/2 method is not at all suitable for the analysis of molecular bonding whatsoever, and the fundamental discrepancies apparent in Datta (1976), and Datta and Datta (1978) may now be mentioned (i) these authors have neglected interference density and related properties through the localized molecular orbitals. But it is not *a priori* clear how the interference effect which arises due to the wave-like behaviour of fundamental particles (Ruedenberg 1962) is incorporated in a zero-order orbital framework. However, Nakatsuji (1974) showed how interference

obtained from the delocalized set of Ransil (1966). On the other hand, Layton Jr and Ruedenberg (1964) studied the chemical binding in the same system by the same method using the same wave function of Ransil. But it is apparent that the corresponding values of Datta are different from that of Layton Jr and Ruedenberg, and the same wavefunction (evaluated at the equilibrium distance) has been used over a range of 21 distances of internuclear separation—the reason for which are not mentioned in the paper (iii) Datta and Datta (1978) have calculated interference density at the bonding region through CNDO/2 functions. But interference effect cannot arise here because of the orthogonal nature of the basis functions, which cannot be changed by the unitary transformation converting the delocalized set into a localized one. Thus, the work is not consistent with the basic philosophy of CNDO/2 formalism.

However, Shillady *et al* (1971) noted that a CNDO/2D formalism, in which the orbitals from the CNDO/2 calculations are deorthogonalized by Löwdin (1950) transformation, gives charge distribution that follows closely the trend of *ab initio* calculations, and McIver *et al* (1971) noted that the charge density distribution found by such a method is comparable with experimental results. Since the basis set is not orthogonal, the overlap distribution ($Aa \cdot Bb$) and the overlap integral $S(Aa Bb)$ are no longer zero and the inclusion of interference effect is theoretically justified in CNDO/2D formalism. We have therefore, undertaken a CNDO/2D study of charge distribution, in terms of orbital and overlap population, in H_3B-NH_3 and H_3B-CO as compared to the available *ab initio* results. We have also computed one-particle density, interference density at the bond mid-point and the kinetic part of the interference energy, the bond population as functions of internuclear separation between the donor and the acceptor to study the variation of covalent binding with internuclear distance by the same method. The two-centre energy term, E_{A-B} , and one of its components for the new bond are computed, to use as bond index, by CNDO/2 energy partitioning.

2. Method of computation

The geometric parameters of the donors, the acceptor and the adducts are optimized by CNDO/2 method using standard parameters and STO basis set. The overlap and coulomb integrals are evaluated from the explicit expressions derived by Roothaan (1951). The B-L bond is made to coincide with Z (C_3) axis of the coordinate system. The CNDO/2 density matrix is deorthogonalized according to Löwdin's prescription (Löwdin 1950)

$$P' = S^{-1/2} P S^{-1/2} \quad (15)$$

where P and P' are the density matrices corresponding to orthogonal and non-orthogonal bases, and S is the overlap matrix over Slater orbitals respectively. P' is used to calculate charge distribution through equations (4) and (5). The computed orbital populations, and CNDO/2 vis-a-vis CNDO/2D charge distribution of all the chemical species at CNDO/2 equilibrium geometry are shown in table 1 and figure 1 respectively. The orbital pairwise decomposed B-N, B-C and C-O bond populations are shown in tables 2-4 respectively. The acceptor and the donor moieties are kept at geometry to which they are reorganized in the adducts and a series of wavefunctions are calculated

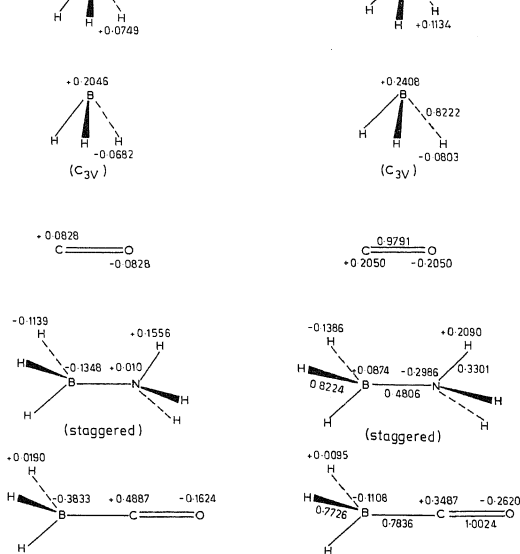


Figure 1. Charge distribution in the donors, the acceptor and the adduct.

and mid-point, and T^I , the kinetic part of the interference energy, is calculated by the formula

$$\begin{aligned}
 T^I &= \int \hat{T} \rho^I(R) dR \\
 &= \sum_{Aa} \sum_{Bb} P(Aa Bb) \int \hat{T} \langle Aa Bb \rangle dR \\
 &= \sum_{Aa} \sum_{Bb} P(Aa Bb) T \langle Aa Bb \rangle,
 \end{aligned} \tag{16}$$

where $\hat{T}$ is the operator for kinetic energy and the integral $T \langle Aa Bb \rangle$ is the kinetic energy of the orbital interference density (equation (11)).

$$T \langle Aa Bb \rangle = [T(Aa Bb) - \frac{1}{2} S(Aa Bb) \{T(Aa Aa) + T(Bb Bb)\}], \tag{17}$$

AO	Donors and Acceptors	Adducts	
	BH ₃ (C _{3v})	BH ₃ -NH ₃	BH ₃ -CO
B _{2s}	1.0488	0.9361	0.9144
B _{2p_x} , B _{2p_y}	0.8272	0.7771	0.8143
B _{2p_z}	0.0560	0.4222	0.5680
H _{1s} (B)	1.0803	1.1386	0.9905
	NH ₃		
N _{2s}	1.6311	1.5057	
N _{2p_x} , N _{2p_y}	1.0244	1.1170	
N _{2p_z}	1.6600	1.5588	
H _{1s} (N)	0.8866	0.7910	
	CO		
C _{2s}	1.7416		1.3980
C _{2p_x} , C _{2p_y}	0.5453		0.6435
C _{2p_z}	0.9627		0.9664
O _{2s}	1.8633		1.8585
O _{2p_x} , O _{2p_y}	1.4547		1.5350
O _{2p_z}	1.4322		1.3336

Table 2. Breakdown of the B-N bond population (BH₃-NH₃).

Orbital pairs	Populations
B _{2s} /N _{2s}	-0.0125
B _{2s} /N _{2p_z}	0.0658
B _{2p_x} /N _{2s}	0.1925
B _{2p_z} /N _{2p_z}	0.2050
π(B _{2p_x} /N _{2p_x})	0.0150
π(B _{2p_y} /N _{2p_y})	0.0150

Table 3. Breakdown of the B-C bond population (BH₃-CO).

Orbital pairs	Populations
B _{2s} /C _{2s}	-0.0077
B _{2s} /C _{2p_z}	0.0556
B _{2p_z} /C _{2s}	0.3426
B _{2p_x} /C _{2p_z}	0.1677
π(B _{2p_x} /C _{2p_x})	0.1127
π(B _{2p_y} /C _{2p_y})	0.1127

where the matrix elements are given by

$$T(Aa Bb) = \int Aa(R) \hat{T} Bb(R) dR, \quad (1)$$

Orbital pairs	Populations	
	(a)	(b)
C_{2s}/O_{2s}	-0.2110	-0.0992
C_{2s}/O_{2p_z}	0.0753	0.2267
C_{2p_z}/O_{2s}	0.0706	-0.0464
C_{2p_z}/O_{2p_z}	0.4221	0.3804
$\pi(C_{2p_x}/O_{2p_x})$	0.3110	0.2704
$\pi(C_{2p_y}/O_{2p_y})$	0.3110	0.2704

(a) Free CO at the same geometry as in H_3B-CO ; (b) CO moiety in H_3B-CO .

$$T(Bb Bb) = \int Bb(R) \hat{T} Bb(R) dR. \quad (20)$$

The $T(Aa Bb)$ elements are computed through the explicit formulae of Roothaan (1951). In computing ρ the entire basis set is included, but in computing ρ^i the principal interacting orbitals of B, N and C only are considered. The two-centre energy terms E_{A-B} for bonded interaction are a measure of the strength of chemical bond and have five components (Fischer and Kollmar 1970)

$$E_{AB} = E_{AB}^R + E_{AB}^V + E_{AB}^J + E_{AB}^K + E_{AB}^N, \quad (21)$$

of which E_{AB}^R , the contribution of resonance integrals to the energy of the $A-B$ bond, is the main feature of the covalent bond and closely correlates with the E_{AB} values. The E_{AB} and its E_{AB}^R components are computed for each B-N and B-C separation. The computed values of ρ , ρ^i , T^i , E_{AB} , E_{AB}^R and P_{AB} are shown in tables 5 and 6 for H_3B-NH_3 and H_3B-CO respectively. The orbital pairwise decomposition of ρ^i and the corresponding T^i are shown in tables 7 and 8 for B-N and B-C bonds respectively.

Table 5. $\rho(R)$, $\rho^i(R)$, T^i , E_{A-B} , E_{A-B}^R , and the bond populations at several distances of B-N separation in borazane.

$r(B-N)$, (Å)	$\rho(R)$	$\rho^i(R)$	T^i (a.u.)	E_{A-B} (a.u.)	E_{A-B}^R (a.u.)	B-N bond population
1.165	0.4237	0.0654	-0.0049	-0.7657	-1.4412	0.4222
1.365	0.2837	0.0537	-0.1690	-0.8719	-1.1619	0.4976
1.565	0.1885	0.0419	-0.2603	-0.8119	-0.9133	0.4806
1.765	0.1228	0.0311	-0.2913	-0.6765	-0.6914	0.4189
1.965	0.0771	0.0216	-0.2744	-0.5172	-0.4984	0.3355
2.165	0.0461	0.0140	-0.2281	-0.3196	-0.2921	0.2482
3.50	0.0426	0.0001	-0.0068	-0.0136	-0.0060	0.0051

$r(\text{B-C})$ (Å)	$\rho(R)$	$\rho^I(R)$	T^I (a.u.)	E_{A-B} (a.u.)	E_{A-B}^R (a.u.)	$B-C$ bond populations
1.04	0.3558	0.0810	0.1031	-1.2171	-2.0305	0.8202
1.24	0.2692	0.0579	-0.0416	-1.3772	-1.6987	0.8705
1.44	0.1998	0.0432	-0.1434	-1.2932	-1.3804	0.7836
1.64	0.1456	0.0320	-0.1962	-1.0890	-1.0785	0.6418
1.84	0.1033	0.0237	-0.2122	-0.8492	-0.8080	0.5030
2.04	0.0714	0.0170	-0.2002	-0.6231	-0.5807	0.3797
3.50	0.0023	0.0003	-0.0101	-0.0134	-0.0137	0.0102

R = mid point of $r(\text{B-C})$.

Table 7. The orbital pair-wise breakdowns of the interference density and the corresponding interference kinetic energies at several distances of B-N separation in borazane.

$r(\text{B-N})$, (Å)	$\rho_{2s/2s}^I(R)$	$\rho_{2s/2p}^I(R)$	$\rho_{2p/2s}^I(R)$	$\rho_{2p/2p}^I(R)$	$T_{2s/2s}^I$	$T_{2s/2p}^I$	$T_{2p/2s}^I$	$T_{2p/2p}^I$
1.165	-0.0055	0.0036	0.0110	0.0563	0.0417	-0.0208	-0.0576	0.0318
1.365	-0.0022	0.0061	0.0096	0.0403	0.0178	-0.0442	-0.0779	-0.0646
1.565	-0.0005	0.0057	0.0078	0.0289	0.0046	-0.0509	-0.0862	-0.1278
1.765	0.0002	0.0045	0.0061	0.0203	-0.0019	-0.0498	-0.0841	-0.1556
1.965	0.0004	0.0032	0.0044	0.0137	-0.0045	-0.0429	-0.0745	-0.1525
2.165	0.0003	0.0021	0.0030	0.0086	-0.0051	-0.0338	-0.0598	-0.1294
3.50	0	0.00002	0.00003	0.00007	-0.0002	-0.0009	-0.0017	-0.0040

(R) = mid point of $r(\text{B-N})$.

Table 8. The orbital pair-wise breakdowns of the interference density and the corresponding interference kinetic energies at several distance of B-C separation in carbonyl borane.

$r(\text{B-C})$, (Å)	$\rho_{2s/2s}^I(R)$	$\rho_{2s/2p}^I(R)$	$\rho_{2p/2s}^I(R)$	$\rho_{2p/2p}^I(R)$	$T_{2s/2s}^I$	$T_{2s/2p}^I$	$T_{2p/2s}^I$	$T_{2p/2p}^I$
1.04	-0.0052	0.0039	0.0198	0.0625	0.0388	-0.0171	-0.0552	0.1366
1.24	-0.0018	0.0034	0.0155	0.0408	0.0133	-0.0201	-0.0815	0.0468
1.44	-0.0002	0.0032	0.0127	0.0274	0.0017	-0.0245	-0.0990	-0.0216
1.64	0.0004	0.0026	0.0104	0.0186	-0.0032	-0.0243	-0.1055	-0.0633
1.84	0.0005	0.0021	0.0082	0.0128	-0.0055	-0.0231	-0.1018	-0.0817
2.04	0.0006	0.0017	0.0062	0.0087	-0.0065	-0.0203	-0.0904	-0.0831
3.50	0.00002	0.00003	0.0001	0.0001	-0.0005	-0.0009	-0.0040	-0.0047

(R) = mid point of $r(\text{B-C})$.

3. Results and discussion

The H $\bar{\text{B}}\text{H}$ angle reorganizes to 110° in both the complexes. The B-H bond length is

obtained by several non-empirical methods (Armstrong and Perkins 1969; Etmiller *et al* 1976; Umeyama and Morokoma 1976). The HNH angle changes from 105° to 109.25° , and the N-H bond length (1.07 Å) remains unchanged, on adduct formation. The reorganization energy of NH_3 is negligible (0.0019 a.u.). The optimized B-N bond length 1.565 Å, is in very good agreement with its experimental value 1.56 Å (Shore and Parry 1955; Hughes 1956; Lippert and Lipscomb 1956). The optimized B-C bond length is 1.44 Å which is also in good agreement with its experimental value (Herzberg 1966). The C-O bond stretches from 1.19 to 1.211 Å and the reorganization energy of CO is negligible (0.0019 a.u.). The staggered form of borazane is the stabler one.

3.1 Mulliken population analysis

3.1a Ammonia borane: From figure 1 we see that the CNDO/2D formal charges on B in $\text{BH}_3(\text{C}_{3v})$ is positive and that on N in NH_3 is negative and these formal charges do not change appreciably on molecular formation although, 0.3284 a.u. of charge has been formally transferred from the donor to the acceptor. But the formal charges on all the H atoms changes significantly on adduct formation. The charge density on H attached to B changes from -0.0803 a.u. to -0.1386 a.u. and that on H attached to N changes from +0.1134 a.u. to +0.2090 a.u. Since B is nearly neutral and N is strongly negative in the complex, the charge rearrangement contradicts the classical belief of the formation of the dative bond by the donation of lone pair of electron of N to the empty orbital of B. From table 1 we see that the population in B_{2p_z} orbital increases considerably and those in all the other B orbital decreases, while in N, the charge donating atom, the populations in $2s$ and $2p_z$ orbitals decrease and those in $2p_x$ and $2p_y$ orbitals increases. The overlap population of the B-N bond is surprisingly low compared to those of B-H and N-H bonds. Table 2 demonstrates that the $\text{B}_{2s}/\text{N}_{2s}$ overlap population is a negative number (antibonding) and the B-N bond is essentially constructed from $2p_\sigma$ orbital of B and $2s$ and $2p_\sigma$ orbitals of N, and the major contributors are the $2p_\sigma$ orbital pair. Thus the charge transfer originates mostly from the N_{2p_z} orbital to the B_{2p_z} orbital and a charge readjustment finally takes place between the two central atoms and the H atoms bound to them to make N atom strongly negative and B atom virtually uncharged. This same pattern of charge distribution and bond formation in this molecule were found by several *ab initio* calculations (Veillard *et al* 1967; Moireau and Veillard 1968; Armstrong and Perkins 1969). On the other hand, CNDO/2 method overestimates the net transfer of charge (0.4765 a.u.) and gives positive charge on N and negative charge on B (figure 1), which was also noted by Shillady *et al* (1971). Moreover, the bond formation cannot be studied by CNDO/2 method.

3.1b Carbonyl borane: Figure 1 demonstrates that the formal charges on C of CO and B of BH_3 are positive. Thus the formation of $\text{BH}_3\text{-CO}$ involves the joining of two positively charged fragments. The net balance of charge transfer is 0.08 a.u. of electronic charge from CO moiety to the BH_3 moiety. These two facts suggest that, during the process of bond formation, both the interacting groups act in a concerted way to donate and accept charge. On adduct formation, the B atoms are formally negatively charged while the H atoms are positively charged, and the formal positive charge on C and negative charge on O are increased. Table 1 demonstrates that the population in $\text{B}(2p_z)$

2s and $2p_z$ orbital of C. Thus the charge donation stems from the 2s and $2p_z$ orbitals of C into the $2p_x$ orbital of B and as a final adjustment charge migrates from O(2s) and O($2p_z$) orbitals into C(2s) and C($2p_z$) orbitals. The amount of charge migrated from B(2s) orbital must be donated to the H atoms. Since the magnitude of $\pi(\text{B-C})$ population is considerable and the electron density around H atoms is decreased, the back-donation of charge from BH_3 to CO must be taking place through the 'hyperconjugative' mechanism as suggested by Graham and Stone (1956). The p-orbitals of B, C and O atoms have simultaneous overlap with the group orbitals of three H atoms to drift charge around H towards C and O. Thus Mulliken's categorisation of CO as an 'amphodonor' is also supported by this CNDO/2-*D* calculation.

One more interesting point to note is the dramatic increase in C-O bond population on adduct formation (figure 1), which may be offered as a natural explanation of the spectroscopic observation of the increase in CO stretching frequency on complex formation with BH_3 (Bethke and Wilson 1957; Taylor 1957; Sundaram and Cleveland 1960; Cowan 1949, 1950). The breakdowns of the bond populations of the free CO at the same geometry as in the complex, and of CO in the complex into orbital pairwise components (table 4) show that the observed increase in the C-O bond population arises from the reduction of the large antibonding $\text{C}_{2s}/\text{O}_{2s}$ population and from an increase of $\text{C}_{2s}/\text{O}_{2p_z}$ population on complex formation. This pattern of charge redistribution within the donor and the acceptor and the mechanism of bond formation were also observed by several *ab initio* calculations (Armstrong and Perkins 1969; Runtz and Bader 1975; Kato *et al* 1974; Ermler *et al* 1976; Uneyama and Morokuma 1976). Although the gross patterns of charge rearrangement are the same in both CNDO/2 and CNDO/2-*D* methods, the former over-estimates the net transfer of charge (figure 1).

3.2 The one-particle density, the interference density and the kinetic interference energy, and other bond indices.

The quantities in tables 5 and 6 have a common trend of variation. The binding interaction starts at a sufficiently large R , the distance of internuclear separation between the atoms forming the new bond. The bond-populations, one-particle density and the interference density at the bond mid-point steadily grow as R decreases, indicating a piling of charge density in the bonding region in both the systems. The E_{AB}^R , the resonance integral, steadily decreases with decrease of R , while E_{AB} , the energy of the newly formed bond, closely correlates with the A-B bond-population and passes through a minima at shorter R where the latter is maximum. It is further noted that the sum of the reorganization energies of the donor and the acceptor is over-compensated by the energies of the newly formed bond in both the systems over a considerably large range of internuclear separation.

The kinetic interference energy T^I starts with a negative value at large R and sharply decreases with the decrease in R , and then rapidly increases below R_e , the equilibrium R , for both the systems under study. However, T^I remains negative over the entire range of study in $\text{H}_3\text{B-NH}_3$, and becomes positive at shorter R values below R_e in $\text{H}_3\text{B-CO}$. The plot of T^I versus R functions of R (figure 2) shows that the kinetic interference

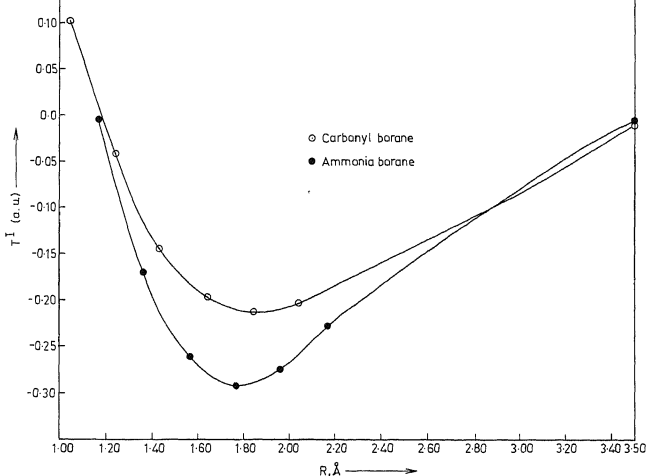


Figure 2. Plot of the kinetic interference energy as a function of internuclear distance.

general pattern of the kinetic component of Morse curve (Slater 1933; Eyring *et al* 1944). According to the kinetic component of the Morse curve, kinetic energy decreases as R decrease and then increases rapidly as the nuclei are brought closer together. Ruedenberg (1962) argued that such lowering of kinetic energy comes through interatomic interference, and he conjectured that due to cluster promotion atoms form the promotion states in which potential energy is decreased and kinetic energy is excessively increased leading to an overall promotion, and subsequent interference causes a large compensating lowering in kinetic energy. At larger R , cluster promotion is less important and pure interference effect is possible to lower the kinetic energy, but at shorter R , particularly at and around R_e , cluster promotion is important and therefore kinetic energy should start increasing. Although there is no scope of inclusion of cluster promotion in the present calculation, the general trend of variation of T^I values with R is consistent with the experimental curve of variation in kinetic energy as function of internuclear separation (the kinetic component of Morse curve).

The interference density of $2s(B)/2s(N)$ orbital pair is positive (bonding) at larger R values and negative (antibonding) at and below R_e (table 7). The corresponding kinetic energy component $T^I_{2s/2s}$ is consistent with the nature of interference, negative at larger R values and positive at shorter R values. This orbital pair, therefore, has a binding

density is constructed by $2p/2p$ orbital pair followed by that of $B(2p)/N(2s)$ pair at all R . The corresponding kinetic energy components reveal that the interference interaction due to all these orbital pairs starts with a binding effect from a large R and grow steadily with decreasing R , and then increases at further closer approaches. The $T_{2s/2p}^I$ and $T_{2p/2s}^I$ components pass through a minima at R_e while the minima of the $T_{2p/2p}^I$ component is above R_e , and increases very sharply at shorter R values indicating a stronger localisation of electron near the nuclei. However, starting from large R up to R_e the major fraction of the interference energy is contributed by the $2p/2p$ orbital pair followed by that of $B(2p)/N(2s)$ orbital pair, signifying that the B-N bond is principally formed due to electron sharing by $2p_\sigma$ orbital of B with $2s$ and $2p_\sigma$ orbitals of N.

Table 8 demonstrates that $B(2s)/C(2s)$ orbital pair creates a constructive interference at longer R and a destructive interference at and below R_e . The antibonding effect of this orbital pair is also noted in population analysis (table 3). The corresponding kinetic energy component $T_{2s/2s}^I$ is consistent with the nature of interference i.e. it is negative at larger values and positive at and below R_e . The interference densities due to other orbital pairs increase monotonically with decrease in R and $2p$ orbitals, followed by $B(2p)/C(2s)$ pair, construct the major fraction of interference density. The corresponding kinetic energy components, however, behave dissimilarly with those of borazane system. The $T_{2s/2p}^I$ and $T_{2p/2s}^I$ components decrease first, pass through minima, then increase with the decrease of R . The $T_{2p/2s}^I$ and $T_{2p/2p}^I$ components decrease hand in hand at larger R values, but at shorter R values the latter increases very sharply and becomes positive. The sharper increase in the kinetic energy components of $2p$ orbital pair in this system may be due to the much closer approach of the interacting groups. Thus, the B-C bond is principally formed by $2p_\sigma$ orbital of B, and $2s$ and $2p_\sigma$ orbital of C.

One more point to be discussed is the kinetic energy components of $2p$ orbital pairs below R_e . These quantities are positive at shorter distances below R_e in spite of the positive interference density of these orbital pairs (tables 7, 8). A closer look at the definition of kinetic interference energy (equations (16) and (17)) shows that the sign of this quantity depends on the signs of the element of bond order matrix and the integral $T\langle Aa Bb \rangle$. The latter and not the former, should be very sensitive of R . Although the atomic quantities $T(Aa Aa)$ and $T(Bb Bb)$ remain constant at all R because of non-inclusion of cluster promotion in the present calculation, $T(Aa Bb)$ and $S(Aa Bb)$ change with R to reverse the sign of the integral $T\langle Aa Bb \rangle$ at shorter distances below R_e .

4. Conclusion

Thus we see that CNDO/2D calculation has reproduced the trend of charge distribution, in terms of orbital and overlap populations, of the *ab initio* method in H_3B-NH_3 and H_3B-CO fairly well. The CNDO/2 bond indices E_{AB} and E_{AB}^R , and CNDO/2-D derived quantities like P_{AB} , ρ , ρ^I and T^I all indicate the binding situation as functions of internuclear separation. E_{AB} and E_{AB}^R are semi-empirical quantities while ρ is a very useful tool for studying various chemical phenomena (McWeeny 1954; Bamzai and Deb 1981) and ρ^I is a fundamental quantity for covalent binding. The variation of T^I

the numerical results obtained were consistent with the concepts associated theoretical quantities. The CNDO/2-D method, therefore, appears to be a good a to extract useful information on chemical binding.

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Reaction of the carbonate radical with substituted anilines

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Abstract. Rate constants for the reaction of carbonate radical with aniline and some para-substituted anilines have been determined by the flash photolysis technique. Using $\sigma + \rho_{\text{para}}$ values the rate constants at pH 8.5 correlate very well with the Hammett equation yielding $\rho = -1$. The carbonate radical oxidises aniline giving the anilino radical. The products so formed have been identified through studies under conditions of continuous irradiation.

Keywords. Flash photolysis; carbonate radical; rate constants; substituted anilines.

1. Introduction

The carbonate radical ($E_{\text{red}}^0 = 2.1 \text{ V}$) (Endicott 1975) can react with aromatic substrates through direct electron transfer or through an electrophilic addition or substitution (Ross and Neta 1979; Chen *et al* 1975). The reaction of the carbonate radical with a series of para-substituted anilines has been examined with a view to obtain indications about the mechanism.

2. Experimental

2.1 Materials

The complex $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{ClO}_4$ is prepared according to literature procedure (Rochow 1960; Chen *et al* 1973). All the anilines were purified by recrystallisation. In the case of liquid substances, freshly-distilled samples were used for preparing solutions. For flash photolysis experiments the pH of the solutions was adjusted using KH_2PO_4 and NaOH and for continuous photolysis studies NaOH alone was used for adjusting the pH.

2.2 Measurements

Flash photolysis experiments were carried out using a 10 cm quartz cell in a Nortech flash photolysis unit type FPX-1 and the transient was recorded using data display system type DFR-2 (Nortech Laboratories, England) combined with a chart recorder (Siemens Kompensograph 111). The flash lamps dissipated up to 200 J of energy with a half peak duration of about 30 μsec . The decay of the carbonate radical was monitored by following the absorbance at 600 nm and measurement made at $23 \pm 1^\circ\text{C}$. All

solutions were prepared with triply-distilled water and deaerated with purified N_2 before flashing. However, it was found that dissolved oxygen has no effect on the kinetic data. Only freshly-prepared solutions were used for flash photolysis studies to exclude possible thermal reaction and were discarded after a single flash.

2.3 Product analysis

Product analysis studies were carried out by continuous photolysis with a 48 W low pressure Hg vapour lamp (Rayonet RUL 2537 A). Before the carbonatotetramine-cobalt(III) salt is used as a source of carbonate radical for continuous irradiation studies, experiments were conducted leaving the reaction mixture in the dark and it was noticed that in dark this Co(III) complex oxidises aniline slowly. In order to further minimise their reaction, the solution is well cooled and the complex salt is added at the last moment before irradiation. After irradiation the products are immediately extracted with ether. In a typical experiment, a solution containing 10^{-2} M complex and 10^{-3} M aniline at pH 8.5 is irradiated for 30 min after deaeration with purified N_2 or Ar. The residue from the ether extract is separated and identified by TLC. 4-aminodiphenylamine, azobenzene and benzidine are the major products and 2-aminodiphenylamine and hydrazobenzene are formed in trace amounts. In addition, phenylhydroxylamine is also formed. Azobenzene is formed by the rapid oxidation of hydrazobenzene. Therefore in these experiments azobenzene was identified as a major product and hydrazobenzene as a minor product. UV spectrum of these separated products compared well with that of authentic samples. The separated amines are also mixed with *p*-dimethylaminobenzaldehyde and the visible spectra of the resulting derivatives (Zechner *et al* 1976) compared well with those of authentic samples. Under these conditions aniline itself without added complex underwent photolysis yielding the same products, except phenylhydroxylamine, but in considerably reduced yields. In mixtures the Co(III) complex is the major absorber of the radiation and not aniline. At 254 nm, the extinction coefficients for cobalt(III) complex and aniline are found to be 11340 and $669 \text{ M}^{-1} \text{ cm}^{-1}$ respectively. In the dark the complex plus aniline gets slowly oxidised at 40°C to give phenylhydroxylamine and the products such as 4-aminodiphenylamine, hydrazobenzene, etc which were isolated in photolytic conditions were conspicuously absent. These results show that the greater yield of 4-aminodiphenylamine, azobenzene, benzidine and 2-aminodiphenylamine that are obtained on irradiating the carbonatotetraminecobalt(III) complex with aniline result from the reaction of the carbonate radical with aniline.

3. Results

The carbonate ion radical is produced on flashing a solution containing about $2 \times 10^{-5} \text{ M} [\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{ClO}_4$ by charge transfer to metal (CTTM) transition (Cope and Hoffman 1972; Chen *et al* 1973).

order in the absence of any scavenger (decay constant $2 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$) and becomes pseudo-first order in the presence of added scavenger. This pseudo-first order rate constant is determined at least three different initial concentrations of scavenger and at each concentration at least four kinetic curves were processed. Second order rate constants were determined from the slope of the plots of the pseudo-first order rate constants *vs* [scavenger] (figure 1). The rate constants obtained for aniline and some parasubstituted anilines at pH 8.5 are given in table 1. These data are subject to an error inherent in flash photolysis studies ($\pm 10\%$).

The effect of pH on the rate constant for the reaction of carbonate ion radical with aniline is studied. The rate constant remains almost constant in the pH range 6–11.

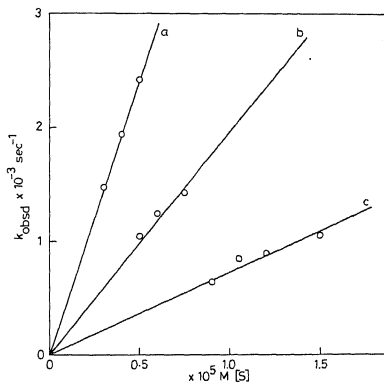


Figure 1. Dependence of k_{obs} on scavenger concentration at pH = 8.5, a. aniline b. *p*-aminobenzoic acid c. *p*-nitroaniline.

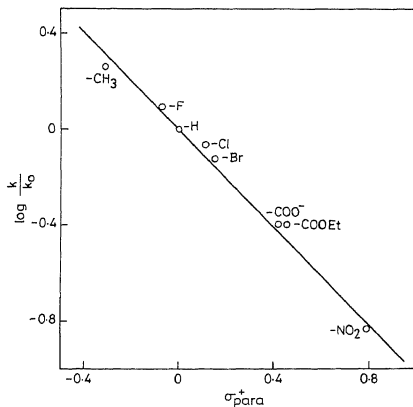
Table 1. Rate constants for the reaction of $\text{CO}_3\text{H}^\cdot$ with aniline and *p*-substituted anilines (pH = 8.5).

Scavenger	$k_2 \text{ M}^{-1} \text{ sec}^{-1}$
Aniline	5.0×10^8
<i>p</i> -chloroaniline	4.3×10^8
<i>p</i> -bromoaniline	3.8×10^8
<i>p</i> -aminobenzoic acid	2.0×10^8
<i>p</i> -aminoethylbenzoate	2.0×10^8
<i>p</i> -nitroaniline	7.3×10^7

independence of the rate constant shows that the intrinsic reactivity of CO_3H^- and CO_3^{2-} towards aniline is the same.

4. Discussion

To understand the effect of substituent on the reactivity of aniline with carbonate radical the rate constants given in table 1 are correlated with appropriate Hammett substitution constants. With σ_p^+ values (Brown and Okamoto 1958) a good correlation is obtained (figure 2). The ρ value of -1 obtained is similar to that observed for the reaction of carbonate ion radical with substituted phenols (Moore *et al* 1977). Crable and Kearns (1962) found that the ionization potentials of the *p*-substituted anilines correlate well with σ_p^+ values. Thus it is possible that the rate constants are influenced by the ionization potentials of the amine suggesting possible electron transfer from aniline to the carbonate radical. Attempts were therefore made to observe the possible anilino-radical intermediate. Since the pK_a of the anilino radical $\text{C}_6\text{H}_5\text{NH}_2^+$ is 7 (Land and Porter 1963), at pH 8.5 it deprotonates to give $\text{C}_6\text{H}_5\text{NH}^\cdot$. For the protonated and basic forms of the anilino radical, absorption maxima of 423 and 300 nm respectively have been reported by Land and Porter (1963). When a solution containing $3 \times 10^{-5} \text{ M}$ $[\text{CO}(\text{NH}_3)_4\text{CO}_3]\text{ClO}_4$ and $2 \times 10^{-5} \text{ M}$ aniline at pH 8.5 is flashed with about 125 J of energy there is very little absorption in the 423 nm region and the absorption around 300 nm could not be followed due to limitations of

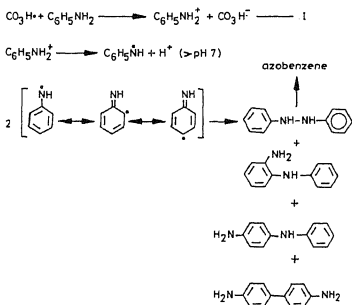


the smaller flash energy. Since the pK_a value of the bicarbonate radical is 9.6 ± 0.3 at both pH 6 and 8.5 the bicarbonate radical will exist mainly in the protonated form $\text{CO}_3\text{H}^\cdot$. Hence at pH 8.5 also the formation of $\text{C}_6\text{H}_5\text{NH}_2^+$ is expected but will immediately deprotonate to give $\text{C}_6\text{H}_5\text{NH}^\cdot$ which dimerises to give hydrazobenzene and other observed products (scheme 1).

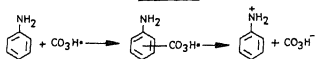
Though the σ_p^+ values correlate very well with IP of substituted aniline, figure 2 cannot be taken as a definite indication of the mechanism of the reaction, *i.e.* electron transfer or radical attachment. The $\rho\sigma_p^+$ correlation has also been applied to electrophilic aromatic substitution (Exner 1972) and step 1 of scheme 1 may involve the intermediacy of an adduct (scheme 2).

The adduct could rearrange by an overall electron transfer mechanism to give the anilino radical. Since no specific transient other than anilino radical could be observed in the region 350–650 nm, the formation and collapse of the adduct may be very rapid and these two processes may be completed before any observation could be made. It is believed that such an adduct may indeed exist since a similar reactivity for both the forms of the radical towards aniline has been observed. If a direct electron transfer mechanism were operating, then one would expect the uncharged protonated form $\text{CO}_3\text{H}^\cdot$ to be a stronger oxidising agent and thus to react more rapidly in an electron transfer process than CO_3^- . However both forms could show similar reactivity if H abstraction or addition modes were operative.

SCHEME - 1



SCHEME - 2



aniline to give both cyclohexadienyl type radical and anilino radical. The less reactive $\text{CO}_3\text{H}^\cdot$ radical is more selective and gives only anilino radical.

The reaction of carbonate radical with aliphatic amines is also studied and the constants are found to be two or three orders lower than those for aniline. These constants do not give a satisfactory correlation with their ionization potentials. With amines like RCH_2NH_2 products like RCHO are identified, probably formed by α -hydrogen abstraction. Detailed studies of these systems are in progress.

5. Conclusion

It may be concluded that carbonate radical oxidises aniline to anilino radical. Anilino radical containing electron donating *p*-substituents have higher rate constants at pH 7 compared to unsubstituted aniline whereas the converse is observed for anilino radical containing electron withdrawing *p*-substituents.

Acknowledgement

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Boron complexes of sulphur containing Schiff bases derived by the condensation of S-methyl or S-benzyl dithiocarbazate with β -diketones

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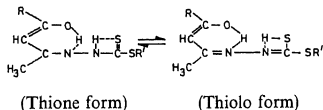
Abstract. Tetra-coordinated boron derivatives, $(\text{EtO})\text{B}(\text{DTZ})$ and $(\text{DTZH})\text{B}(\text{DTZ})$, (where DTZ^{--} and DTZ^- represent the anions of the Schiff base DTZH_2) have been synthesized by 1:1 and 1:2 molar reactions of triethoxyborane with bibasic tridentate Schiff bases, derived by the equimolar condensation of S-methyl or S-benzyl dithiocarbazate with acetyl acetone or benzoyl acetone. Further 1:1 derivatives have been shown to undergo replacement reactions with *t*-butyl alcohol, showing thereby the labile nature of the ethoxy group. Based on infrared and proton magnetic resonance spectral studies and monomeric nature, suitable structures have been assigned to these derivatives.

Keywords. Boron complexes; dithiocarbazate derivatives; Schiff bases; ^1H NMR spectra; IR spectra.

1. Introduction

Extensive studies on the transition metal complexes of dithiocarbazate Schiff bases have been carried out and a review featuring their geometry and configurations has also appeared (Ali and Livingstone 1974). However, similar investigations concerning the non-transition element complexes are scanty (Pardhy *et al* 1980; Agarwal *et al* 1980). In earlier communications (Singh *et al* 1980; Singh and Tandon 1977) a variety of boron derivatives with nitrogen donor ligands have been reported and some of these have been found to possess considerable biological activity (Singh and Tandon (unpublished)). Recently, the physiological aspects of boron complexes have also been reviewed (Niedenzu 1979).

Some new boron derivatives having B-S bond, are synthesized by the reactions of triethoxyborane with the Schiff bases having the donor system HSNOH and which may be structurally represented as follows:



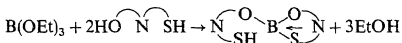
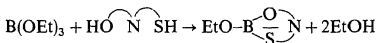
I, $R = -\text{CH}_3$, $R' = -\text{CH}_3$ (AcAcMTZH_2)

II, $R = -\text{CH}_3$, $R' = -\text{CH}_2\text{C}_6\text{H}_5$ (AcAcBTZH_2)

III, $R = -\text{C}_6\text{H}_5$, $R' = -\text{CH}_3$ (BzAcMTZH_2)

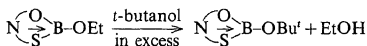
IV, $R = -\text{C}_6\text{H}_5$, $R' = -\text{CH}_2\text{C}_6\text{H}_5$ (BzAcBTZH_2)

The desired products are obtained by 1:1 and 1:2 molar reactions of triethoxyborane with the ligands AcAcMTzH₂, AcAcBTzH₂, BzAcMTzH₂, BzAcBTzH₂. However, a 2:3 molar reaction simply yielded a mixture of the products formed by 1:1 and 1:2 molar reactions. The 1:1 product could be isolated using a mixture of benzene and *p*-xylene. These reactions were quite facile due to the weaker B-OR bonding as well as the reactive nature of the dithiocarbazate Schiff bases (Ali and Livingstone 1974).



(where HO $\begin{array}{c} \curvearrowright \\ \text{N} \\ \curvearrowright \end{array}$ SH represents the donor system of bibasic tridentate Schiff base).

The 1:1 products further undergo replacement reactions with *t*-butyl alcohol as indicated below:



The resulting products are obtained as coloured, nonvolatile and highly viscous liquids or solids. These are soluble in common organic solvents, monomers and unstable in the open atmosphere probably due to the weaker B-S bond.

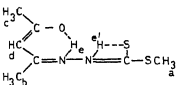
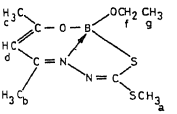
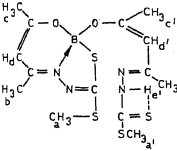
2.1 IR spectra

The IR spectra of the Schiff bases in solid form display strong bands at 1500 and 1050 cm⁻¹ assignable to $\nu_{\text{C-N}}$ and $\nu_{\text{C=S}}$ respectively Sahni and Kapoor (1979). These bands support the presence of the thione form; however, in solution spectra in ethanol, both these bands disappear and a sharp band at ~ 2570 cm⁻¹ is observed due to SH which is indicative of the thiol form. These studies probably indicate that the -NH-C=S group exists mainly in the solid form, whereas in solution an equilibrium exists between the two tautomeric forms.

A strong band appears in the region, 3200–3125 cm⁻¹ due to the hydrogen bonded $\nu_{\text{OH}}/\nu_{\text{NH}}$ which is not observed in the 1:1 boron derivatives, due to the deprotonation of OH/NH group and the chelation of oxygen to boron. However, in the spectra of the 1:2 derivatives the characteristic band of NH is observed indicating that one of the functional groups of at least one Schiff base does not undergo deprotonation.

The shifting of the frequency due to azomethine stretch $\nu_{\text{C=N}}$ to the higher side, (~ 1600 cm⁻¹–1630 cm⁻¹) in the boron derivatives is probably due to an increase in the C=N bond order after the formation of N → B bond (Samuel *et al* 1970). All these derivatives show a strong band at ~ 1540 cm⁻¹ which may be due to the $\nu_{\text{B-N}}$ as reported earlier (Wang *et al* 1970). The $\nu_{\text{B-O}}$ (asym) appears at ~ 1310 cm⁻¹ in all the boron derivatives (Singh *et al* 1980).

2.2 NMR spectra

Compound	a (a')	b (b')	c (c')	d (d')	e (e')	f	g
	2.10	2.40	2.56	5.83	10.75	—	—
	2.21	2.94	2.61	6.28	—	3.53	1.13
	2.38 (2.18)	2.92 (2.43)	2.57 (2.64)	6.13 (5.78)	10.52 (4.26)	—	—

(δ) ppm for the various protons are listed in table 1 and the following points appear to be significant from the structural point of view: (i) In 1 : 1 derivative, the disappearance of hydroxyl (δ 10.75 ppm) and thiole proton signal (δ 4.45 ppm) shows chelation of boron through both oxygen and sulphur atoms, whereas in 1 : 2 derivative the appearance of the thiole proton signal at δ 4.25 ppm, clearly indicates that at least in one of the ligand moieties one functional group remains unbonded. (ii) In 1 : 1 derivative, the methine proton and one of the methyl proton (labelled d and b respectively in table 1) signals show downfield shifting leaving behind two methyl proton (labelled a and c table 1) signals almost unchanged. This may be due to the boron acquiring a tetracoordinated state after accepting a lone pair of electrons from the azomethine nitrogen. (iii) In 1 : 2 derivative, however, two sets of proton signals are observed for every proton. One set remains at almost the same position as in the ligand, thereby showing that one of the ligands is acting as tridentate and another one as unidentate as shown in table 1.

3. Experimental

A glass apparatus fitted with quickfit interchangeable joints was used and the reactions

Triethoxyborane was prepared by refluxing boric acid (S. Merck) with absolute ethanol in dry benzene (BDH) and removing water azeotropically (Lippincott). It was distilled before use and analysed: Found: B, 7.44; OC_2H_5 , 91.97%. Calcd. for $\text{B}(\text{OEt})_3$: B, 7.41; OC_2H_5 , 92.59%.

S-methyldithiocarbamate and S-benzoyldithiocarbamate were prepared as reported earlier (Ali *et al* 1971; Ali and Bose 1977). To prepare the Schiff bases, a weighed amount of S-methyl- or S-benzyl dithiocarbamate was dissolved in ethanol and mixed with an equimolar amount of β -diketone (ethanolic solution). The reaction mixture was kept over a water bath for about 10 min and left overnight at room temperature. The crystals which separated out were filtered off and recrystallized from the same solvent.

3.2 Analytical methods and physical measurements

Boron was estimated as reported earlier (Singh and Tandon 1977). Nitrogen was determined by the Kjeldahl's method and the sulphur was analysed by the literature method (Saraswat *et al* 1977). Carbon and hydrogen were analysed by the carbon hydrogen analyzer (Coleman-5602). Ethanol liberated in the reactions was estimated oxidimetrically (Bradley *et al* 1950). Molecular weight was determined ebullioscopically in boiling benzene using thermistor sensing.

IR spectra were recorded in Nujol mulls on a Perkin Elmer 577 grating infrared spectrophotometer and PMR spectra were scanned in carbon tetrachloride (using TMS as internal standard) on a Perkin-Elmer RB-12 spectrometer.

3.3 Synthesis of boron Schiff base complexes

A weighed amount of triethoxyborane was mixed with the calculated amount of Schiff base in dry benzene (~ 75 ml). The reaction mixture was refluxed over a fractionating column and the ethanol liberated was collected azeotropically with benzene. The completion of the reaction was ascertained by the ethanol estimation. After its complete removal, the excess of the solvent was distilled off and the products dried under reduced pressure (2 mm) for 2 hr. Further details are listed in table 2.

3.4 Exchange reactions of boron Schiff base derivatives

t-Butanol in excess was mixed with dry benzene solution of ethoxyboron Schiff base derivatives and the reaction mixture was refluxed over a ratio head. The ethanol was collected azeotropically with benzene and the rest of the procedure was the same as described in §3.3.

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Reduction mechanism of 1,4-diamino-2,3-anthraquinone disulphonic acid

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Abstract. The potentiometric acid constants of 1,4-diamino-2,3-anthraquinonedisulphonic acid were calculated. The sequence of dissociation is discussed. The reduction of the reagent at a dropping mercury electrode has been investigated. The polarograms of reagent show two waves, whose adsorption and diffusion nature is respectively established. The reaction orders, together with Tafel's slopes have been calculated.

Keywords. Anthraquinones; polarography; potentiometry; reduction mechanism

1. Introduction

The diaminoanthraquinones are selective and sensitive reagents suitable for spectrophotometric and fluorimetric determination of a good number of metallic ions (Krausz *et al* 1963), but no attention seems to have been paid yet to their electrochemistry. 1,4-diamino-2,3-anthraquinonedisulphonic acid has been previously studied with respect to some analytical applications and has been proposed for the spectrophotometric determination of Au(III) (Capitán *et al* 1977), Pd(II) (Capitán *et al* 1982) and as an acid-base indicator (Capitán *et al* 1978).

In this paper the potentiometric dissociation constants are determined and the reduction of this reagent on a mercury electrode is studied.

2. Experimental

1,4-diamino-2,3-anthraquinonedisulphonic acid was synthesized according to Pattison's patent (Pattison *et al* 1957) by condensing 1,4-diamino-2,3-dichloroanthraquinone with boric acid and sulphuric acid to form a boric acid ester complex. The excess acid is neutralized and sodium sulfite added, replacing thus the chlorine atoms with sulphonic groups when heated at about 95°–100°C. The reagent was identified by elemental analysis, IR and NMR.

The acid-dissociation constants of reagent have been determined by the potentiometric Bjerrum's (1941) method at ionic strength $\mu = 0.1$, from the titrations of the free acid, monosodium salt and disodium salt performed with a Metrhom-Herisau E-536 potentiograph.

The *i*-*E* curves were registered either automatically or traced point by point using a

471 Amel multipurpose unit with the damping circuit completely suppressed. The cyclic voltammetry curves were recorded on a Tektronix ssp 3 polarograph. The potentials were measured *vs.* SCE with a Radiometer PHM-84 potentiometer which was also used as a pH-meter.

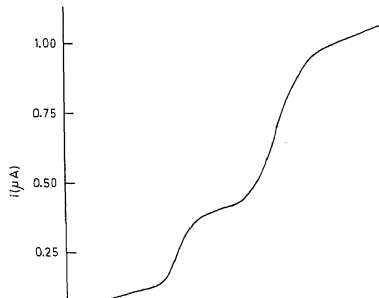
The polarographic measurements were made using a thermostated Amel 494 cell. A saturated calomel reference electrode was used. The working electrode was a mercury capillary with the following characteristics: rate of mercury flow $m = 1.95$ mg/sec, drop time $t = 5.15$ sec, open circuit, in a buffered solution at pH 12.15 and the height of the mercury column $h = 42.50$ cm. The cyclic voltammetry curves were found out using a hanging drop electrode as working electrode.

All the reagents used were Merck AR grade. As a supporting electrolyte solution, a buffered solution of 6.66×10^{-2} M Na_3PO_4 and 0.1 M. H_3PO_4 mixed in varying proportions according to the pH desired was used. The ionic strength was adjusted with KNO_3 to 0.24 M. All the measurements were done in an atmosphere of nitrogen and at a temperature $25.0 \pm 0.1^\circ\text{C}$.

3. Results

The acid-dissociation constants of 1,4-diamino-2,3-anthraquinonedisulphonic acid were determined potentiometrically (Bjerrum 1941) at ionic strength $\mu = 0.1$. A maximum of two dissociation constants have been determined in the range of pH investigated and their pK values are $\text{pK}_1 = 3.91$ and $\text{pK}_2 = 8.15$.

The 1,4-diamino-2,3-anthraquinonedisulphonic acid reduced on the DME produce two polarographic waves from aqueous solutions at concentrations smaller than 1.6×10^{-3} M. Both waves were always observed throughout the complete pH range studied (2.00–12.71). Figure 1 shows a representative polarogram at pH 12.50 $(E_{\frac{1}{2}})_1 = -0.616$ V, and $(E_{\frac{1}{2}})_2 = -0.848$ V.



current on the height of the mercury column and the temperature. Thus the adsorption and diffusive nature of the first and the second wave respectively were proved (Zumr 1969).

The dependence of the half-wave potential on pH was studied as well, to determine how many hydrogen ions are involved in the reduction. Polarograms were recorded for 2×10^{-4} M solutions in the pH range 5.60–12.72. $E_{1/2}$ and n values were calculated in each case. Figure 2 shows the plots of $E_{1/2}$ vs pH. One can observe two straight lines with slopes of which are 62 mV and 28 mV depending on whether pH is lower or higher than 8.27. Accordingly, the number of hydrogen ions involved in the reduction must be either $p = 2$ or $p = 1$ respectively.

On the other hand, we checked whether the limiting currents are proportional to the concentration of the 1,4-diamino-2,3-anthraquinonedisulphonic acid in the bulk of the solution, in the range 5×10^{-3} M– 4×10^{-5} M at pH 12.50. The values of the slopes of the linear segments are: $1.65 \mu\text{A/L/mM}$ and $3.10 \mu\text{A/L/mM}$ for the first and the second wave respectively. Hence, the diffusion current constants are $I = i_d/m^{2/3} t^{1/3}$, $C = 607 D^{1/2} n = 1.51$ calculated for the second wave, and the diffusion coefficient is $D = 1.55 \times 10^{-6} \text{ cm}^2/\text{sec}$. Such I and D values agree with those previously published for some anthraquinone (Capitán *et al* 1979, 1980, 1981).

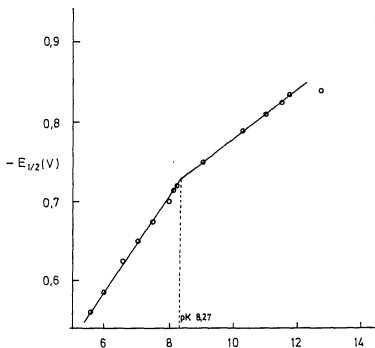
The half-wave potentials $E_{1/2}$ remains independent with an increase in concentration.

The transfer coefficient determined from Tafel's slope is $\alpha = 0.48$ and the order of reaction with respect to the concentration is:

$$\left| \frac{d \log i}{d \log C} \right|_E = 1$$

calculated from the second wave.

We carried out controlled potential microcoulometry to determine n , i.e., the number of electrons involved in the reduction. It appears that the reduction



concentration were registered showing always two cathodic peaks and one anodic peak respectively. The main observed features are:

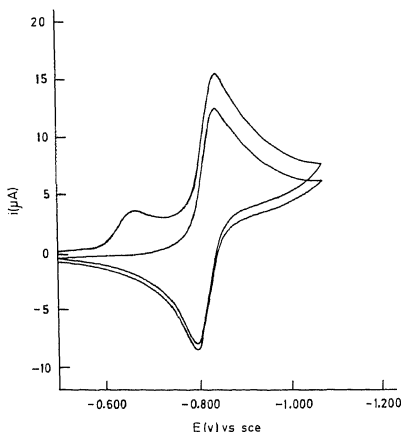
(a) Successive voltammograms obtained at different sweep rates show that the first wave disappears when a second cycle is imposed immediately after the first and the sweep rate is higher than 20 mV/sec (figure 3). This confirms the adsorption nature of the first wave. Such behaviour has been observed by Ali-Qureshi *et al* (1979) for a similar reagent.

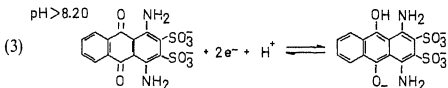
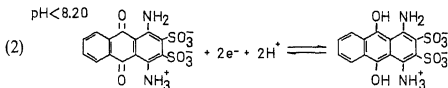
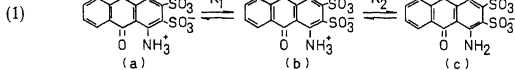
(b) The cathodic (positive) and anodic (negative) peak currents for the second wave are virtually identical; the peak separation $E_{P(c)} - E_{P(a)}$ being 33 mV, which is not far from the theoretical value of 30 mV for a bielectronic transference. Hence, one can say that the reduction of reagent is reversible under such conditions. On the other hand the plots of i_p vs. $\log v$ at different concentrations are linear with slopes of 0.5, in agreement with theoretical value.

(c) The α and reactions order values calculated from this technique agree with those previously calculated polarographically.

4. Discussion

The acid dissociation constant values obtained potentiometrically as well as the strong acidic nature of the sulphonic groups (being thus extensively dissociated) suggest that in





aqueous solution the 1,4-diamino-2,3-anthraquinonedisulphonic acid is structured mainly as in scheme 1a. Owing to its structure, (a) is a rather strong acid ($\text{pK}_1 = 3.91$) and it may be easily dissociated to give the structure as in scheme 1b. Finally it can dissociate ($\text{pK}_2 = 8.15$) to give a structure as in scheme 1c.

These dissociation steps agree with those found for similar molecules (García-Sánchez *et al* 1970).

Moreover, here, the polarographic curves show that the reduction of the 1,4-diamino-2,3-anthraquinonedisulphonic acid proceeds by one bielectronic step diffusion controlled in basic medium, showing specific adsorption of the reagent at the mercury electrode. The reagent requires two electrons and two protons at pH lower than 8.20 and two electrons and one proton at pH higher than 8.20, to produce the respective hydroquinone. The shape of the cyclic voltammetry curves is, in agreement with the diagnostic criteria proposed for a EE mechanism at the investigated scan rates.

From the results and conclusions obtained and in accordance with the dissociation steps of the reagent, we propose for the reduction of 1,4-diamino-2,3-anthraquinonedisulphonic acid, a mechanism with the following reaction pathways: (a) At pH lower than 8.20 the predominant form is as in scheme 1b, which captures two electrons and two protons to form a hydroquinone system. (scheme 2). (b) At pH higher than 8.20 the predominant form is as in scheme 1c, which captures two electrons and one proton to form a hydroquinone system (scheme 3).

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Spectral, magnetic and thermal studies of transition metal complexes of δ (3-carboxy, 4-hydroxy benzoyl) pentanoic acid

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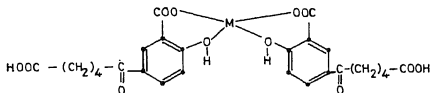
MS received 30 August 1982; revised 24 December 1982

Abstract. Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) form 1 : 2 complexes while Fe(III) forms 1 : 3 complex with δ (3-carboxy, 4-hydroxy benzoyl) pentanoic acid. Their structures have been proposed on the basis of analytical, spectral, thermal and magnetic measurements. The infrared spectra provide an evidence for the replacement of the aromatic carboxylic group hydrogen but not the phenolic group hydrogen.

Keywords. δ (3-carboxy, 4-hydroxy benzoyl) pentanoic acid; salicylic acid; transition metal complexes

1. Introduction

In recent years metal carboxylates have attracted considerable attention in chemistry because of their importance in industry and their interesting structure (Bassi *et al* 1980). Inoue *et al* (1964) reported magnetic moment of Cu(II) salicylate. Koppikar and Soundararajan (1976) studied diiodosalicylates of rare earths. A large number of derivatives of salicylic acid with metal halides have been reported (Goyal and Khosla 1980). However no study of transition metal complexes of δ (3-carboxy, 4-hydroxy benzoyl) pentanoic acid has been reported so far. Hence this study.



(M = Cu²⁺, Co²⁺, Ni²⁺, Mn²⁺, and Zn²⁺)

2. Experimental

2.1 Preparation of pentanoic acid

Polyphosphoric acid (50 g) was added to a mixture of salicylic acid (0.05 mol, 6.9 g) and adipic acid (0.075 mol, 10.95 g). After mixing, the reaction mixture was heated at 110°C for 4 hr. The solid obtained was added to the ice-cold water, filtered and washed with hot water. It was purified by dissolving in 10% alkali solution and precipitated as a brownish green coloured compound with ice cold 10% HCl. It is soluble in alcohol with a melting point of 150°C.

2.2 Preparation of complexes

The complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Fe(III) were prepared by mixing the solution of metal chloride in water and solution of $\delta(\text{CHB})$ PA in absolute alcohol in a stoichiometric 1 : 2 molar ratio (metal : ligand) for bivalent metal ions and 1 : 3 for Fe^{+3} . Precipitates were obtained by addition of sodium acetate. The complexes were washed with hot water and ethanol.

2.3 Elemental analyses

Carbon and hydrogen were microanalysed by Coleman carbon hydrogen analyzer.

2.4 Metal content in the complexes

Known amounts of the metal complexes were decomposed with AR conc. HCl , HNO_3 , HClO_4 and H_2SO_4 . The residue was cooled, dissolved in water and made up to a known volume in a volumetric flask. All the metal ions were determined by EDTA titration using appropriate indicator.

2.5 Physical measurements

Magnetic susceptibility of the complexes at room temperature was determined by Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. Molar susceptibilities were corrected for diamagnetism of the constituent elements using Pascal's constants. The IR spectra of ligand and complexes were recorded in the form of KBr pellet on UR-10 spectrophotometer in the range $3600\text{--}400\text{ cm}^{-1}$. Diffuse reflectance spectra in the solid state were obtained from a Beckman DU spectrophotometer using MgO as reference. TG data were obtained from an assembly capable of producing temperatures up to 800°C with a heating rate 10° min^{-1} .

3. Results and discussion

The important thermal, spectral and magnetic moment data of the complexes are summarised in table 1. The infrared spectra provide important information about the attachment of ligand to the metal ions. IR spectra of all the metal complexes show absorption characteristic of the asymmetric (at 1600 cm^{-1} as compared to 1670 cm^{-1} in free ligand) $\nu_{\text{as}}\text{COO}$ for coordinated carboxylate group attached to the aromatic ring (Mishra and Jha 1980). The broad band observed in the ligand due to phenolic $-\text{OH}$ reduced from $2500\text{--}3600\text{ cm}^{-1}$ to $3300\text{--}3600\text{ cm}^{-1}$ in complexes indicating removal of hydrogen bonding (Garg *et al* 1971). The IR spectral studies thus suggest that aromatic carboxylic group hydrogen is replaced and the phenolic group remains in tact.

The analytical data agree with the general formula ML_2 (where M = bivalent metal ions) and ML_3 (where $\text{M} = \text{Fe(III)}$). TGA data show that the decomposition of the complexes starts at 200°C (Cu), 250°C (Ni), 260°C (Co), 250°C (Mn), 260°C (Zn) and 220°C (Fe) and complete decomposition of the organic material takes place at $550\text{--}660^\circ\text{C}$ leaving a

Compound	Decomposition Temp (°C)	μ_{eff} (BM)	Energies	Transition
δ (CHB) PA	220			
Cu [δ (CHB) PA] ₂	200	2.00	14285	$^2B_{1g} \rightarrow ^2B_{2g}$
Ni [δ (CHB) PA · H ₂ O] ₂	250	2.71	8770	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$
			14290	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$
			22222	$^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$
Co [δ (CHB) PA] ₂	260	3.86	8000	$^4A_2 \rightarrow ^4T_1(F)$
			16667	$^4A_2 \rightarrow ^4T_1(P)$
Mn [δ (CHB) PA] ₂	250	4.42	20000	$^6A_1 \rightarrow ^4T_1(G)$
				$^6A_1 \rightarrow ^4T_2(G)$
				$^6A_1 \rightarrow ^4E_1, ^4A_1(G)$
Fe [δ (CHB) PA] ₃	220	4.84	20000	$^6A_{1g} \rightarrow ^4A_{1g}, ^4E_g$
			14285	$^6A_{1g} \rightarrow ^4T_{2g}$
			12500	$^6A_{1g} \rightarrow ^4T_{1g}(G)$
Zn [δ (CHB) PA] ₂	260	Diamagnetic	—	

moment to spin only value (1.73 BM) might be due to orbital contribution (Baker *et al* 1966). The magnetic susceptibility data wants detailed examination because of the low values obtained in the case of Ni(II), Co(II), Mn(II) and Fe(III) complexes. Ni(II) complex shows a magnetic moment of 2.71 BM which is lower than the spin only value. This may be due to the octahedral distortion (Rastogi and Sharma 1974). Cobalt(II) complex exhibits magnetic moment of 3.86 BM which is lower than that expected for regular tetrahedral Co(II) complexes. The subnormal magnetic moment may be due to the covalent nature of the metal ligand bonds (Sengupta *et al* 1981). The room temperature magnetic moment of the Mn(II) complex is 4.42 BM which does not conform well with the spin only moment expected for the spin free configuration. The low value of magnetic moment may be due to aerial oxidation of Mn(II) $\rightarrow$ Mn(III) during preparation. However, some workers explain this low magnetic moment on the basis of antiferromagnetic interaction between manganese(II) ions in solid state (Patel and Patil 1982). The effective moment of the Fe(III) complex is 4.84 BM which is quite lower than the spin only value of 5.92 BM for high spin d^5 system. Subnormal magnetic moment can be interpreted in terms of antiferromagnetic behaviour (Syamal and Kale 1980). In most cases the electronic spectrum of Cu(II) complex possesses only a single broad band, making the assignment of individual electronic transition difficult (Patel *et al* 1981). A broad band at 14285 cm^{-1} is observed which may be assigned to $^2B_{1g} \rightarrow ^2B_{2g}$ transition for square planar stereochemistry (Patel *et al* 1981). Nickel(II) complex shows bands at 8770 cm^{-1} (ν_1), 14290 cm^{-1} (ν_2) and 22222 cm^{-1} (ν_3) which may be assigned to $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ transitions respectively for distorted octahedral stereochemistry (Lever 1968). The value of B (Racah inter-electronic repulsion parameter) was calculated using the method suggested by Konig (1971). The calculated values of B , β and CFSE are found to be 680 cm^{-1} , 0.629 and 30.08 kcal/mol respectively. The ratio ν_2/ν_1 (1.60) supports distortion in octahedral stereochemistry (Arora and Misra 1982). The reflectance

to be 895.8 cm⁻¹, 0.80 and 12.8 kcal/mole respectively. Manganese (II) complex exhibits a broad absorption band at 20000 cm⁻¹ which may be assigned to the group of three lowest energy bands as ${}^6A_1 \rightarrow {}^4T_1$ (G), ${}^6A_1 \rightarrow {}^4T_2$ (G) and ${}^6A_1 \rightarrow {}^4E$, 4A_1 (G) for tetrahedral stereochemistry (Forster and Goodgame 1964). In Fe(III) complex three bands are observed at 20000, 14285 and 12500 cm⁻¹ attributable to ${}^6A_{1g} \rightarrow {}^4A_{1g}$, 4E_g , ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G) transitions for octahedral stereochemistry (Srivastava *et al* 1974). The Zn(II) complex is diamagnetic and may have a tetrahedral structure.

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Polarographic study of the complexes of cadmium(II) and lead(II) with methoxyacetate ions

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Abstract. Reduction of the complexes of cadmium(II) and lead(II) at DME in aqueous and aqueous-methanol media at $\mu = 1.0 \text{ M} (\text{NaClO}_4)$ at 15 ± 0.1 and $25 \pm 0.1^\circ\text{C}$ is reversible and diffusion-controlled. Four complex species are formed in either case. The overall stability constants of 1:1, 1:2, 1:3 and 1:4 complexes have been determined. Lead(II) complexes are much stronger than the corresponding cadmium(II) complexes.

Keywords. Polarography; cadmium; lead methoxyacetate.

1. Introduction

Recently, the plant auxins such as 3-indoleacetate, 3-indole-butyrate, and 1-naphthaleneacetate have been reported to form weak complexes with trace elements cadmium(II), zinc(II), manganese(II) and thallium(I) (Parkash *et al* 1981, 1983). Since fungicide action is also an important phenomenon occurring in plants, it was considered worthwhile to study the interaction of methoxyacetate, a fungicide, with trace elements cadmium(II) and lead(II) at DME in aqueous and aqueous-methanol mixture media.

2. Experimental

Cadmium nitrate tetrahydrate (E Merck, AG), lead nitrate (BDH, AnalaR), sodium perchlorate monohydrate (E Merck, GR), perchloric acid (Reidel) and Triton-X-100 (Rohms and Hass Co.) were used. All the other chemicals used were of guaranteed purity. Triple-distilled mercury and double distilled water were used. Methanol was purified and distilled before use (Vogel 1959). Methoxyacetic acid was prepared from sodium methoxide and freshly-distilled chloroacetic acid (Blatt 1946) and purified by distillation under reduced pressure ($96.5^\circ\text{C}/13 \text{ mm}$) b.p. $203\text{--}204^\circ$. Structure and purity of the acid was further confirmed by its PMR spectrum.

Stock solutions of cadmium(II) and lead(II) were prepared in water and standardized (Welcher 1959). Sodium salt of methoxyacetic acid was prepared and pH of this stock solution was adjusted using ELICO pH meter model LI-10. Solutions containing metal ions ($4 \times 10^{-4} \text{ M}$) and varying concentrations of the complexing agent ($0.0\text{--}0.9 \text{ M}$) were prepared in water and 10% methanol media at ionic strength 1 M maintained with sodium perchlorate.

gas presaturated with the background solution to be polarographed, was used for deaeration and an inert atmosphere was maintained over the solution during electrolysis. The electrolysis was carried out in a H-cell in conjunction with an agar-agar plug saturated with sodium chloride. Polarograms of 0.4 mM cadmium(II) and lead(II) solutions were obtained in the presence of different concentrations of methoxyacetate at 15 ± 0.1 and $25 \pm 0.1^\circ\text{C}$ using REDELKIS polarograph type OH-102 in aqueous and 10% methanol media. Triton-X-100 (0.002% in the final solution) was used as maxima suppressor whenever required. An *iR* compensation was used while working with methanolic solutions. The currents were corrected for residual current. The resulting polarographic data as a function of the ligand concentration (C_x) which was calculated from the pH of the solution and pK_a value of the ligand (3.55 at 15°C , 3.57 at 25°C (King 1960)), are given in table 1.

3. Results and discussion

Both cadmium(II) and lead(II) give single well-defined reversible polarographic reduction wave. Current is directly proportional to $(h_{\text{eff}})^{1/2}$ showing that the reduction is diffusion-controlled. Plot of E_{de} vs $\log i/i_d - i$ is a straight line with a slope of 32 ± 1 mV. Cathodic reduction of cadmium(II) and lead(II) in methoxyacetate is, therefore, reversible and involves two electron transfer in either case. That $E_{1/2}$ is

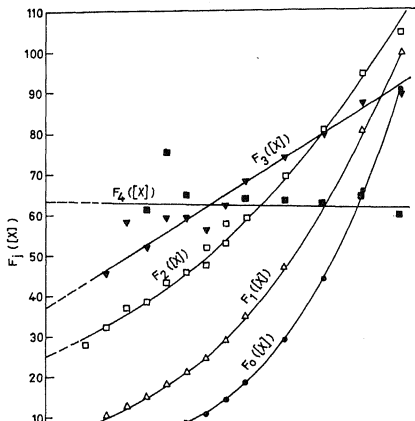
Table 1. Polarographic data of the interaction of cadmium(II) and lead(II) with methoxyacetate ions.

C_x	p^X	Cadmium(II)-methoxyacetate system in						Lead(II) methoxyacetate system			
		aqueous medium at		10% methanol medium at		25 $\pm$ 0.1 $^\circ\text{C}$		in aqueous medium at			
		25 $\pm$ 0.1 $^\circ\text{C}$		15 $\pm$ 0.1 $^\circ\text{C}$		25 $\pm$ 0.1 $^\circ\text{C}$		25 $\pm$ 0.1 $^\circ\text{C}$		15 $\pm$ 0.1 $^\circ\text{C}$	
M		$E_{1/2}$ (-V)	i_d (μA)	$E_{1/2}$ (-V)	i_d (μA)	$E_{1/2}$ (-V)	i_d (μA)	$E_{1/2}$ (-V)	i_d (μA)	$E_{1/2}$ (-V)	i_d (μA)
0.0000	—	0.5800	1.872	0.5865	1.584	0.5695	1.733	0.3755	2.088	0.3810	1.992
0.0200	1.699	0.5810	1.814	0.5885	1.464	0.5725	1.570	0.3855	2.047	0.3905	1.934
0.0500	1.301	0.5825	1.800	0.5920	1.459	0.5770	1.546	0.3965	1.824	0.3985	1.934
0.0999	1.000	0.5860	1.680	0.5970	1.428	0.5838	1.464	0.4025	1.872	0.4100	1.728
0.1499	0.824	0.5895	1.584	0.6010	1.392	0.5890	1.440	0.4145	1.853	0.4160	1.680
0.1999	0.699	0.5945	1.661	0.6045	1.356	0.5943	1.450	0.4210	1.862	0.4215	1.618
0.2499	0.602	0.5980	1.632	0.6080	1.363	0.5985	1.416	0.4250	1.824	0.4250	1.363
0.2998	0.523	0.6015	1.560	0.6108	1.344	0.6025	1.392	0.4290	1.781	0.4280	1.176
0.3498	0.456	0.6050	1.555	0.6130	1.272	0.6060	1.356	0.4330	1.728	0.4345	1.416
0.3998	0.398	0.6080	1.546	0.6160	1.272	0.6100	1.392	0.4360	1.651	0.4380	1.354
0.4497	0.347	0.6115	1.536	0.6183	1.262	0.6135	1.380	0.4400	1.651	0.4405	1.248
0.4997	0.301	0.6148	1.519	0.6205	1.272	0.6155	1.320	0.4425	1.560	0.4430	1.145
0.5996	0.222	0.6205	1.488	0.6250	1.224	0.6213	1.308	0.4485	1.560	0.4485	1.056
0.6996	0.155	0.6255	1.440	0.6298	1.248	0.6265	1.248	0.4540	1.512	0.4540	1.114
0.7995	0.097	0.6300	1.368	0.6325	1.152	0.6310	1.200	0.4588	1.440	0.4595	1.145
0.8995	0.046	0.6335	1.296	0.6355	1.128	—	—	0.4600	1.157	0.4630	0.984

independent of the effective height of mercury column (h_{eff}) is in keeping with the reversible character of the electrode process. There is an appreciable cathodic shift in the $E_{1/2}$ with increase in ligand concentration in either case. The diffusion current also decreases with increasing concentration of the complexing agent due to increase in the size of Cd(II) and Pb(II) ions on complex formation.

$F_o(X)$ functions are calculated at different concentrations of the ligand (DeFord and Hume 1951) and then solved for the stability constant by a graphical procedure, depicted for cadmium as a typical example, in figure 1, which confirms the formation of four consecutive complexes, 1:1, 1:2, 1:3 and 1:4 in equilibrium with each other in either case, having stabilities for the cadmium-methoxyacetate complexes $\beta_1 = 5, 13, 17$; $\beta_2 = 25.5, 29, 67$, $\beta_3 = 37, 20.5, 108.5$ and $\beta_4 = 63.48, 40.25, 149.4$ at $25 \pm 0.1, 15 \pm 0.1^\circ\text{C}$ (both in aqueous medium) and $25 \pm 0.1^\circ\text{C}$ (in 10% methanol) respectively; for lead-methoxyacetate complexes in aqueous medium $\beta_1 = 70, 80$; $\beta_2 = 450, 200$; $\beta_3 = 210, 900$ and $\beta_4 = 1120.96, 861.79$ at 25 ± 0.1 and $15 \pm 0.1^\circ\text{C}$ respectively. Lead(II) complexes with methoxyacetate could not be studied in methanol medium due to precipitation of the complexes formed. The values of overall stability constants calculated by Mihailov's method (1974) are in close agreement with those calculated by DeFord and Hume's method.

Percentage distribution of cadmium(II) and lead(II) present in various forms in equilibrium as a function of logarithm of ligand concentration has also been calculated and a typical figure (figure 2) for distribution diagrams of this type is given.



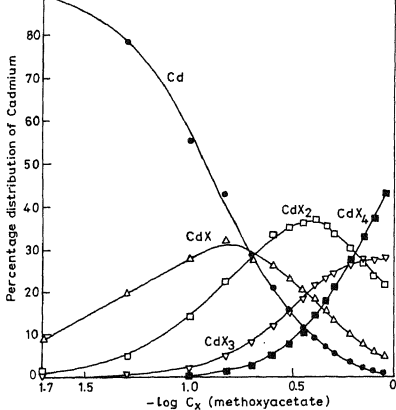


Figure 2. Percentage distribution of cadmium in various forms as a function of $-\log C_x$ in aqueous medium at $25 \pm 0.1^\circ\text{C}$.

It is evident from the results that the complexes formed are more stable at lower temperatures or in methanol medium. However, the highest complex becomes less stable in both cases on lowering the temperature. The lead(II)-methoxyacetate complexes are, in general, more stable than the corresponding cadmium(II) complexes.

Acknowledgement

One of the authors (RB) is thankful to UGC, New Delhi for the award of a fellowship.

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Kinetic studies on the homogeneous hydrogenation of fumaric and maleic acids catalysed by bis(dimethylglyoximate)cobalt(II)

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Abstract. The influence of varying concentrations of $\text{Co}(\text{DMGH})_2$, NaOH and axial base on the rate of hydrogenation of fumaric and maleic acids has been studied in detail. Intramolecular hydrogen bonding in the monoanion of maleic acid and the *trans* orientation of carboxylic acid groups in fumaric acid are important factors which account for the difference in the rate of hydrogenation of these substrates. Mono-, di- and trialkyl amines as axial bases modify the activity of the catalyst, dialkylamines conferring the maximum activity and trialkylamines the least. Back-strain on nitrogen atom and solvation energy of the amines are responsible for their different behaviours. A rate law has been proposed and verified.

Keywords. Cobaloxime; hydrogenation; axial base; fumaric acid; maleic acid.

1. Introduction

Glyoxime complexes of cobalt(II) accept bases in the axial positions to form cobaloximes (Schrauzer 1968; Schrauzer and Windgassen 1970; Schrauzer and Holland 1971; Belluco 1970). Because of the similarity to Vitamin B_{12} in their reactions they serve as excellent models for Vitamin B_{12} (Schrauzer 1976). During the past decade there has been considerable growth in the studies related to the bioinorganic aspects of $\text{Co}(\text{II})$. These studies involve synthesis and reactions of complexes of $\text{Co}(\text{II})$ with dimethyl and other glyoximes, Schiff bases and other macrocyclic ligands. The green $\text{Co}(\text{I})$ species formed by the reduction of cobaloximes have strong reducing properties and nucleophilic character (Dodd and Johnson 1973; Witman and Weber 1977). As a part of our studies on the activation of molecular hydrogen by complexes (Vancheesan *et al* 1978; Rajagopal *et al* 1979; Pillai *et al* 1980, 1982; Thangaraj *et al* 1980) we have investigated the hydrogenation of fumaric and maleic acids by cobaloxime. We report here the results of our studies on the role of (i) orientation of functional groups as in fumaric and maleic acids, (ii) the influence of the axial base in the complex and (iii) the concentration of NaOH on the rate of hydrogenation.

2. Experimental

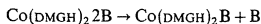
Cobalt chloride hexahydrate and dimethylglyoxime (BDH, AR) were used for the preparation of cobaloxime(III). The catalyst solutions were prepared *in situ* in aqueous

shaking with a saturated solution of ferrous ammonium sulphate (BDH, AR). All cobaloxime solutions were saturated with hydrogen at the reaction temperature prior to the addition of substrates by vigorous stirring till no further hydrogen uptake was observed. The hydrogen absorption was followed at regular intervals by means of a gas burette with provision to maintain a constant pressure of hydrogen. Kinetic studies were carried out by changing any one of the following parameters at a time keeping the others constant: (i) catalyst concentration, (ii) substrate concentration, (iii) axial ligand concentration, (iv) concentration of sodium hydroxide and (v) temperature. Reaction mixtures were withdrawn periodically for product analysis. After separation from the catalyst and other reagents, solid products were analysed by TLC technique using alumina. Liquid samples were analysed by GLC using Varian 1800 model with hydrogen as carrier gas.

3. Results and discussion

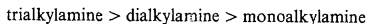
3.1. Effect of axial base

Co(DMGH)₂ forms 1 : 1 and 1 : 2 adducts with a variety of Lewis bases. These adducts are soluble in a number of organic solvents and water. 1 : 2 adducts dissociate in solution.



Under hydrogenation conditions hydrido cobaloximes, HCo(DMG)₂B (DMG = anion of dimethylglyoxime) which are Bronsted acids corresponding to the Lewis bases, are formed. This hydrido species is the catalytic intermediate as in the case of well-known examples of Ru(II), Rh(I), etc. (Hallman *et al* 1968; Osborn *et al* 1966). The stability of the hydridocobaloximes is very much influenced by the axial ligand. σ-donor bases (Schrauzer and Holland 1971). Predominantly σ donor nitrogen bases form unstable hydrido species that cannot be isolated whereas π-acceptors like triaryl and trialkyl phosphines as axial ligands form stable hydrides (Schrauzer and Holland 1971). If the hydride intermediate is too stable, migration of hydride to coordinated substrate becomes difficult, rendering the complex catalytically inactive. On this account pyridine and other N-donor ligands like various substituted amines are considered better axial bases than phosphines for catalytically active complexes. Among several nitrogen-containing compounds (table 1) tried, pyridine was found to be the best. There are several reports of pyridine being a good axial base in cobaloxime catalysis (Simandi 1980; Zahonyi *et al* 1972, 1975).

The catalytic activity of the cobaloxime is attributed to the presence of unpaired electrons in Co(II) which is extensively delocalised along the z axis as indicated by EPR studies (Simandi *et al* 1972, 1975). The result of such delocalisation is an increase in the free radical nature of Co(II), facilitating the interaction with hydrogen through homolytic cleavage of molecular hydrogen. The efficiency of the axial base may be related to the availability of the lone pair. Thus among the mono, di and trialkyl amines the following order of reactivity is expected:

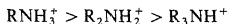


However, the initial rates of hydrogen absorption and percentage conversion to product

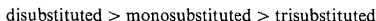
Base	H ₂ absorbed (ml/hr)	% conversion to product
<i>n</i> -butylamine	8.1	33
di- <i>n</i> -butylamine	12.0	46
tri- <i>n</i> -butylamine	nil	nil
Triethyl amine	nil	nil
Trimethyl amine	nil	nil
Pyridine	25	98

* Concentrations of catalyst, substrate, NaOH, axial base and temperature are maintained constant.

reactivity. This deviation from expected reactivity could be attributed to increased back-strain on the N-atom in trisubstituted amines which increases the *p*-character on the lone pair. However, in solution the basicity is increased with the extent of solvation and the solvation energies of the conjugate ammonium ions are in the order:



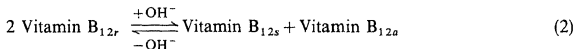
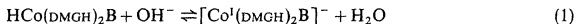
Electronic and solvation effects which oppose each other decide the basicity. As a result dilakylamine has maximum basicity. The difference in basicity is reflected in the activity of the complex for hydrogenation which is in the decreasing order:



With trialkylamines as axial base there was no absorption of hydrogen.

3.2 Effect of alkali concentration

In a strongly alkaline medium (pH > 9), cobaloxime exists predominantly as Co(I) and Vitamin B₁₂ as B_{12s} (equations (1) and (2)) (Schrauzer *et al* 1965; Schrauzer and Windgassen 1966; Hill *et al* 1969).



(In (2) subscripts *s*, *r* and *a* indicate the oxidation states of cobalt.) In Co^I the highest occupied orbital is probably a weakly antibonding *d*_{z² orbital which forms the centre of high polarizability and charge density. Since the equilibrium will be shifted to the right in strongly alkaline medium (equations (1) and (2)) the presence of the acid form HCo^(III) is unlikely (equation (1)). In the presence of H₂ at 1 atmosphere pressure and pH > 9, Co^(I) is a very stable form (Takeuchi and Ohgo 1974). However at pH between 7 and 9, HCo^(III) is the predominant species and the hydrogenation occurs essentially through proton transfer, the mode of addition of substrate being *cis*. However if Co^(I) species reacts with the substrate forming an unstable σ complex, which is subsequently converted to a stable π complex, its further hydrogenation can be effected only under}

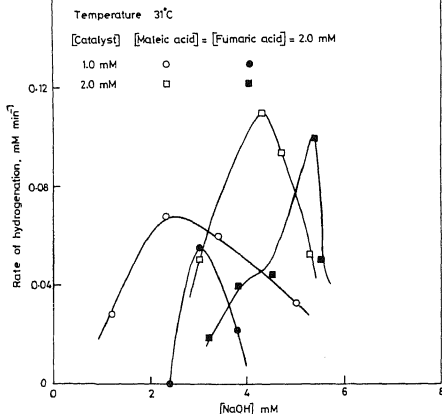
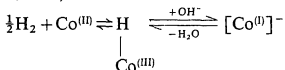


Figure 1. Effect of [NaOH] on the rate of hydrogenation of fumaric acid and maleic acid.

alkaline conditions the active form of cobaloxime is $\text{HCo}(\text{DMGH})_2\text{B}$. Since the substrates used are carboxylic acids, some amount of alkali is used up for neutralizing the acid. The effective $[\text{OH}^-]$ is the excess remaining after neutralisation. On increasing $[\text{OH}^-]$ the rate of hydrogenation passes through a maximum (Shanthalakshmy *et al* 1980). This is in agreement with Schrauzer's scheme where cobaloxime(II) is converted into cobaloxime(III) and cobaloxime(I) (Schrauzer *et al* 1965, 1966, 1968).



This reaction is complete in the presence of excess alkali which explains the steep fall in the rate as the concentration of alkali is increased. The order with respect to catalyst and the substrate is one each and that with respect to $[\text{OH}^-]$ is fractional.

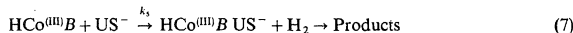
3.3 Nature of the substrate

The rate of hydrogenation of maleic acid was found to be higher than that of fumaric acid. On adding OH^- , maleic acid forms the monoanion which enters into hydrogen bonding with the other carboxyl group which is in close proximity to the carboxylate anion. Hence under the experimental conditions further neutralisation of maleic acid to

Following: (1) the monoanion of maleic acid with an available H⁺ facilitates the formation of hydridocobaloxime(III) which is the active intermediate in the reaction. This is analogous to transfer of hydrogen from a donor solvent to an acceptor *via* hydride intermediate (Pillai *et al* 1980, 1982). The maleate monoanion probably functions as a hydride donor too. This is an additional factor which enhances the rate. In fumaric acid, dianion formation does not leave any scope for the substrate to function as a hydrogen donor. Besides, the *trans* orientation of carboxylate groups is a less favourable geometry for the activation of substrate. This accounts for the difference in the rates of hydrogenation of the two substrates.

3.4 Rate law

The following reaction sequence may be considered.



$$[\text{Co}^{\text{(II)}}B] = K_1[\text{Co}^{\text{(II)}}][B] \quad (8)$$

$$[\text{HCo}^{\text{(III)}}B] = \frac{k_2[\text{Co}^{\text{(II)}}B][\text{H}_2]^{1/2}}{k_{-2} + K_3[\text{OH}^-] + k_5[\text{US}^-]} \quad (9)$$

$$[\text{US}^-] = \frac{K_4[\text{USH}][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (10)$$

Assuming, $\frac{K_4}{[\text{H}_2\text{O}]} = K'_4$, (10) becomes,

$$[\text{US}^-] = K'_4[\text{USH}][\text{OH}^-] \quad (11)$$

$$[\text{HCo}^{\text{(III)}}B] = \frac{k_2 K_1 [\text{Co}^{\text{(II)}}][B][\text{H}_2]^{1/2}}{k_{-2} + K_3[\text{OH}^-] + k_5 K'_4 [\text{USH}][\text{OH}^-]} \quad (12)$$

$$\text{Rate} = k_5 [\text{HCo}^{\text{(III)}}B][\text{US}^-] \quad (13)$$

$$= \frac{k_5 k_2 K_1 K'_4 [\text{Co}^{\text{(II)}}][B][\text{H}_2]^{1/2} [\text{USH}][\text{OH}^-]}{k_{-2} + k_3 [\text{OH}^-] + k_5 K'_4 [\text{USH}][\text{OH}^-]} \quad (14)$$

The observed orders with respect to catalyst and substrate are in agreement with the

denominator in (14) can be neglected, leaving only k_{-2} . At very high $[\text{OH}^-]$, reaction (5) is predominant as discussed earlier. This can be considered to occur *via* formation of $\text{Co}^{\text{II}}\text{B}$ as an intermediate (equation (3)). With increase in $[\text{OH}^-]$, $K_3[\text{OH}^-]$ and $k_5K'_4[\text{USH}][\text{OH}^-]$ increase, since in the denominator of (14), $[\text{OH}^-]$ becomes considerable compared to k_{-2} , causing a steep fall in the rate on increasing $[\text{OH}^-]$. At low $[\text{OH}^-]$, $K_3[\text{OH}^-]$ may be small compared to the rest of the terms in the denominator of (14). Neglecting this and rearranging we get

$$\frac{[\text{Co}^{\text{II}}][\text{B}][\text{USH}]}{R} = \frac{k_{-2}}{k_5K'_4k_2K_1[\text{H}_2]^{1/2}[\text{OH}^-]} + \frac{[\text{USH}]}{k_2K_1[\text{H}_2]^{1/2}}$$

A plot of the left side of the above equation against $1/[\text{OH}^-]$ is almost parallel to the y axis. Hence the term $K_3[\text{OH}^-]$ is included and (14) can be rearranged to give (15)

$$\begin{aligned} \frac{[\text{USH}][\text{Co}^{\text{II}}][\text{B}]}{R} &= \frac{k_{-2}}{k_5k_2K_1K'_4[\text{H}_2]^{1/2}[\text{OH}^-]} + \frac{K_3}{k_5k_2K_1K'_4[\text{H}_2]^{1/2}} \\ &\quad + \frac{[\text{USH}]}{k_2K_1[\text{H}_2]^{1/2}} \end{aligned} \quad (15)$$

If $k_2[\text{H}_2]^{1/2}$ is represented as k'_2 , $k_5k'_2K_1K'_4$ as K and $[\text{Co}^{\text{II}}][\text{B}][\text{USH}]/R$ as A , (15) can be rewritten as

$$A = \frac{k_{-2}}{K[\text{OH}^-]} + \frac{K_3}{K} + \frac{[\text{USH}]}{k'_2K_1} \quad (16)$$

The variation in A as $[\text{OH}^-]$ is changed at constant $[\text{USH}]$ is given by

$$\begin{aligned} \frac{dA}{d[\text{OH}^-]} &= \frac{-k_{-2}}{K[\text{OH}^-]^2} \\ \ln \frac{dA}{d[\text{OH}^-]} &= \ln \frac{-k_{-2}}{K} - 2 \ln [\text{OH}^-] \end{aligned} \quad (17)$$

From the intercept of a plot of left side of (17) against $\ln[\text{OH}^-]$, k_{-2}/K has been evaluated (table 2, figures 2 and 3). In order to evaluate k'_2K_1 , (16) is rearranged after substituting for A and written as (18)

$$\left\{ \frac{[\text{Co}^{\text{II}}][\text{B}]}{R} - \frac{1}{k'_2K_1} \right\} [\text{USH}] = \frac{k_{-2}}{K[\text{OH}^-]} + \frac{K_3}{K} \quad (18)$$

Table 2. Evaluation of some kinetic parameters.

	k_{-2}/K	$k'_2K_1^*$	K_3/K^*	Energy of activation (kcal/mol)
Maleic acid	0.0264	1.19	52.5	17.6
Fumaric acid	0.1114	1.00	100	21.3

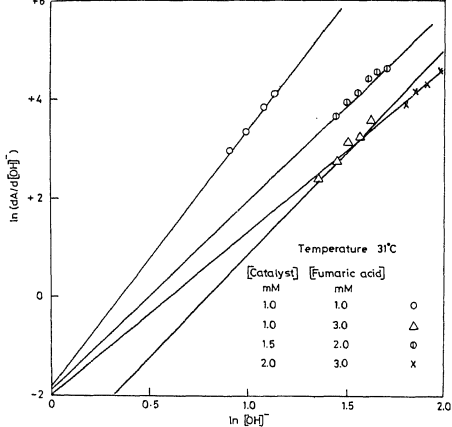
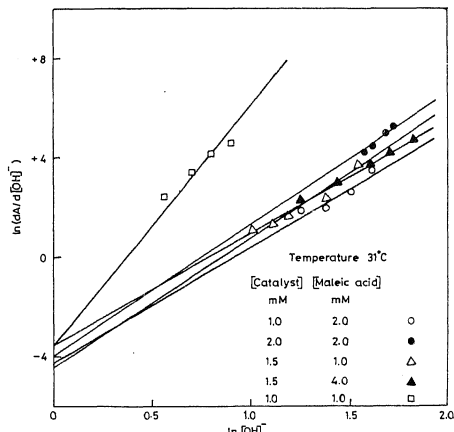


Figure 2. Plot of $\ln(dA/d[OH]^-)$ vs $\ln[OH]^-$ for the evaluation of $-k_2/K_A$ for fumaric acid. Verification of eq. (17).



Differentiating (18) with respect to $[\text{OH}^-]$, we get

$$\left\{ \frac{[\text{Co}^{\text{II}}][\text{B}]}{R} - \frac{1}{k'_2 K_1} \right\} \frac{d[\text{USH}]}{d[\text{OH}^-]} - \left\{ \frac{[\text{Co}^{\text{III}}][\text{B}][\text{USH}]}{R^2} \right\} \frac{dR}{d[\text{OH}^-]} = \frac{-k_{-2}}{K[\text{OH}^-]^2}$$

Rearranging (19) we get

$$\frac{d[\text{USH}]}{d[\text{OH}^-]} = K_1 k'_2 \left\{ \frac{[\text{Co}^{\text{III}}][\text{B}][\text{USH}]}{R^2} \frac{dR}{d[\text{OH}^-]} - \frac{k_{-2}}{K[\text{OH}^-]^2} - \frac{[\text{Co}^{\text{III}}][\text{B}]}{R} \frac{d[\text{USH}]}{d[\text{OH}^-]} \right\} = K_1 k'_2 Q$$

where Q stands for the quantity in flower bracket $\{ \}$ of (20). Q can be calculated the known value of k_{-2}/K and other terms. The linear plot of left side of (20) again passes through the origin and from the slope of this plot, the $K_1 k'_2$ value has been evaluated (table 2). The $K_1 k'_2$ and k_{-2}/K values are substituted in (18) and the value of K_3/K is obtained from the intercept of a plot of left side of (18) against $1/[\text{Co}^{\text{III}}]$. The K_3/K values are given in table 2. The large differences in the k_{-2}/K values are observed for the two acids might be due to the differences in K'_4 (ionization constants of the acids) and k_5 . The lower rate of hydrogenation of fumaric acid compared to maleic acid suggests that k_5 might be small for fumaric acid. The k_{-2}/K and K_3/K values are larger for fumaric acid.

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